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## ANALYTICAL ABSTRACTS

## 1.—GENERAL ANALYTICAL CHEMISTRY

*General reviews of progress, reagents and methods of general application.*

2587. Reports on analytical methods. U.K.A.E.A. Industrial Group, Chemical Services Dept., Springfield. The following reports have been issued by Industrial Group Headquarters, Risley, Warrington, Lancs. Detailed descriptions of the analytical methods are given. Determination of combined nitrogen in zirconium metal, IGO-AM/S-17, 7 pp. Determination of combined nitrogen in titanium metals, IGO-AM/S-20, 6 pp. Gravimetric determination of sulphate in uranium concentrates, IGO-AM/S-129, 4 pp. Absorptiometric determination of copper in beryllium metal, IGO-AM/S-130, 5 pp. Absorptiometric determination of silicon in beryllium, IGO-AM/S-131, 5 pp. Absorptiometric determination of manganese in beryllium metal, IGO-AM/S-132, 4 pp. Absorptiometric determination of iron in beryllium metal, IGO-AM/S-133, 5 pp. Absorptiometric determination of chromium in beryllium metal, IGO-AM/S-134, 5 pp. Absorptiometric determination of nickel in beryllium metal, IGO-AM/S-135, 5 pp. Determination of free carbon in beryllium metal (by ignition, with a gasometric finish), IGO-AM/S-150, 9 pp. Determination of combined carbon in beryllium metal (by ignition, with a gasometric finish), IGO-AM/S-151, 10 pp. Absorptiometric determination of fluorine in beryllium, IGO-AM/S-152, 7 pp. Absorptiometric determination of iron in uranium-molybdenum alloys, IGO-AM/S-160, 5 pp. Spectrographic determination of lithium in magnesium metal, IGO-AM/S-163, 6 pp. Absorptiometric and volumetric determinations of combined nitrogen in beryllium metal (modified Allen method), IGO-AM/S-190, 7 pp. Determination of thorium in thorite ores, IGO-AM/S-193, 14 pp. Gravimetric determination of molybdenum in uranium-molybdenum alloys, IGO-AM/S-202, 5 pp.

2588. Reports on analytical methods. U.K.A.E.A. Production Group, Chemical Services Dept., Operations Branch, Springfield. The following reports have been issued by U.K.A.E.A., Risley, Warrington, Lancs. Detailed descriptions of the analytical methods are given. Spectrographic determination of magnesium in vanadium, PG Report 11 (S), 9 pp. Spectrographic determination of lithium, sodium and potassium in beryllium flake and powder (carrier distillation technique), PG Report 58 (S), 10 pp. Analytical methods for the inspection of ammonia liquor, PG Report 62 (W), 17 pp. Analytical methods for the inspection of hydrazine dihydrochloride, PG Report 63 (W), 14 pp. Analytical methods for the inspection of aluminium nitrate, PG Report 64 (W), 14 pp. Analytical methods for the inspection of sodium nitrite, PG Report 65 (W), 11 pp. Absorptiometric determination of uranium in reactor fuel processing plant solutions (thio-

cyanate procedure), PG Report 66 (W), 5 pp. Analytical methods for the inspection of kerosene, PG Report 67 (W), 16 pp. Analytical methods for the determination of uranium in urine, PG Report 68 (W), 5 pp. Analytical methods for the inspection of nitric acid, PG Report 69 (W), 21 pp. Analytical methods for the inspection of hydrazine mononitrate, P.G. Report 70 (W), 15 pp. Analytical method for the inspection of butex (bis- $\beta$ -butoxyethyl ether), PG Report 71 (W), 25 pp. Analytical method for the inspection of sodium dichromate, PG Report 72 (W), 17 pp. Analytical methods for the inspection of potassium bromate, PG Report 75 (W), 12 pp. Analytical methods for the inspection of hydrochloric acid, PG Report 76 (W), 15 pp. Radiochemical determination of ruthenium-103 and -106 in reactor fuel processing and plant solutions, PG Report 78 (W), 11 pp. Analytical method for the inspection of sulphamic acid, PG Report 80 (W), 15 pp. Analytical methods for the inspection of solid sodium hydroxide and caustic liquor, PG Report 85 (W), 17 pp. Analytical methods for the inspection of iron powder, PG Report 89 (W), 25 pp. Analytical methods for the inspection of potassium bromide, PG Report 90 (W), 14 pp.

2589. Bibliography on analytical flame spectroscopy, 1956 to March, 1959. I. R. Mavrodineanu (Boyce Thompson Inst. for Plant Research, Yonkers, N.Y.). *Appl. Spectroscopy*, 1959, **13** (5), 132-139.—A bibliography of 273 references is presented, the first part of a complete list of 760 references.

II. R. Mavrodineanu. *Ibid.*, 1959, **13** (6), 149-155.—A further 270 references are given.

2590. Trace analysis and its applications. D. Monnier (Lab. de Chim. Min. et Anal., Univ., Genève). *Chimia*, 1959, **13** (10), 314-321.—A review is presented of problems associated with losses, contamination, methods of separation and the sensitivity of different methods of determination. (18 references.) W. T. CARTER

2591. Automation in the field of analytical chemistry. W. Vinaver. *Tech. Mod., France*, 1959, **51** (9), 489-491.—A review.

2592. Anhydrous magnesium perchlorate desiccant with added indicator. G. F. Smith and H. Diehl (Dept. of Chem., Univ. of Illinois, Urbana, U.S.A.). *Talanta*, 1959, **3** (1), 107-108.—Anhydrous  $Mg(ClO_4)_2$  impregnated, by co-crystallisation, with 1 to 2% of  $KMnO_4$  (which is isomorphous with it) is pale purple when dehydrated at 200° to 220°. After absorption of  $H_2O$  the spent reagent becomes dark brown. This reagent is of particular use as a charge for Pregl tubes in elementary microanalysis. J. P. STERN

2593. Potassium trithiocarbonate reagent as a substitute for hydrogen sulphide in inorganic qualitative analysis. K. N. Johri (Dept. of Chem., Univ., Delhi). *J. Sci. Ind. Res., India, B*, 1959, **18**

(10), 430-433.—An 8% aq. soln. of  $K_2CS_2$  (I) (stored under N) precipitates mixtures of metal sulphides and thiocarbonates from acid soln., and thiocarbonates from alkaline soln. This forms the basis of a modified scheme of inorg. qual. analysis. The group-2 metals and Co are pptd. from soln. in HCl at pH 0.7 to 1.0, with methyl violet as external indicator for pH control. The hydroxides of Al, Cr and Fe are separated from the filtrate in the usual way. The filtrate is then rendered alkaline with aq.  $NH_3$  and ammonium carbonate, and the pptd. carbonates of the group-4 metals (Ba, Sr, Ca and Mn) are identified by the chromate-ferrocyanide procedure. Before the pptn. of Zn, Ni and residual Co as thiocarbonates from alkaline soln., Mg is removed by the addition of ethanol. In groups 2 and 5, I is also used to distinguish the sub-groups.

A. ABBOT

2594. Omega chrome blue green BL as analytical reagent for calcium and magnesium. A. A. A. El Raheem and A. S. Moustafa (Public Health Lab. and Nat. Res. Centre, Cairo, Egypt). *Anal. Chim. Acta*, 1959, 21 (4), 379-382.—This dye (C.I. Mordant Green 34) is used as an indicator in the titration of  $Ca^{2+}$  and  $Mg^{2+}$  with 0.01 M EDTA (disodium salt) at pH 10 ( $NH_4Cl$ -aq.  $NH_3$  buffer) in the presence of 2 ml of ethanol or acetone. The colour change is from red to blue, and the end-point is improved by warming the soln. to 60°. Magnesium is also titrated in the presence of  $Al^{3+}$  after adding triethanolamine.

H. N. S.

2595. Analytical use of 8-mercaptoquinoline (thio-oxine) and its derivatives. VII. Internally complexed salts of halogenated 8-mercaptoquinoline and their solubility in organic solvents. Yu. A. Bankovskii and E. F. Lobanova. *Zhur. Anal. Khim.*, 1959, 14 (5), 523-528.—The reaction of thio-oxine (I) and its 3-bromo- (II), 5-bromo- (III) and 6-bromo- (IV) derivatives with metals whose sulphides are stable in water is studied in acid, neutral and alkaline soln. A table summarises the reactions of I, II, III and IV with  $Fe^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Pd^{2+}$ ,  $Mo^{IV}$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Pt^{4+}$ ,  $Ag^+$ ,  $Tl^+$ ,  $Os^{VIII}$ ,  $In^{3+}$ ,  $V^{V}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Ir^{3+}$ ,  $Hg^{2+}$ ,  $W^{VI}$ ,  $Sb^{3+}$ ,  $Bi^{3+}$  and  $Cd^{2+}$ , and gives the solubility and colour of the soln. of the resulting complexes in  $CCl_4$ , benzene,  $CHCl_3$ , isoamyl alcohol and diethyl ether. The solubilities of the complexes in these solvents decrease in the order III, II, I, IV, and are greater in the polar solvents ( $CHCl_3$  and isoamyl alcohol) than in the non-polar solvents (benzene and  $CCl_4$ ). (For Part VI see Bankovskii *et al.*, *Anal. Abstr.*, 1959, 6, 2110.)

C. D. KOPKIN

2596. Studies on di-substituted dithiocarbamates. VII. The stability of diethyldithiocarbamic acids when carbon tetrachloride and chloroform solutions of the diethylammonium diethyldithiocarbamates are shaken with aqueous mineral acids. H. Bode and F. Neumann (Anorg.-chem. Inst., Tech. Hochschule, Hannover). *Z. anal. Chem.*, 1959, 169 (6), 410-416 (in German).—Di-substituted dithiocarbamic acids are rapidly destroyed in acid soln., so that a large excess must be present when a metal complex is to be formed. By using diethylammonium diethyldithiocarbamate in  $CHCl_3$  or  $CCl_4$  soln., the rate of decomposition is reduced. The influence of time of shaking with N HCl and of increasing the concn. of different mineral acids was studied. Nitric acid, HCl and  $H_2SO_4$  caused rapid decomposition at concn.  $>1 N$ ,  $4 N$  and  $10 N$ , respectively.

P. D. PARR-RICHARD

2597. Systematic scheme of qualitative analysis for cations and anions. G. B. S. Salaria (Gov. Coll., Rohtak, Punjab, India). *Anal. Chim. Acta*, 1959, 21 (4), 312-316 (in English).—A system is described in which the initial separation is achieved by boiling the substance with 4 N NaOH and repeating the boiling after the addition of  $Na_2CO_3$ . The scheme covers a large number of acid radicals as well as the commonly occurring metals. H. N. S.

2598. Selected triphenylmethane dyes as acid-base indicators in glacial acetic acid. O. W. Kolling and M. L. Smith (Friends Univ., Wichita, Kans., U.S.A.). *Anal. Chem.*, 1959, 31 (11), 1876-1879.—Several *p*-aminophenyl derivatives of the triphenylmethane series of dyes were examined. The first colour changes of malachite green, brilliant green, Victoria blue and pararosaniline can be used for the titration of strong and intermediate bases with  $HClO_4$  and give an error of  $<3\%$ . Rhodamine B was acceptable in photometric titrations of strong and intermediate bases.

G. P. COOK

2599. Use of brucine as an oxidation-reduction indicator in cerimetry. T. P. Sastri and G. Gopala Rao (Dept. of Chem., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1959, 169 (6), 422-424 (in English).—The use of brucine (I) as an indicator in the titration of  $Fe^{II}$  with  $Ce(SO_4)_2$  has been described (Rao and Sastri, *Anal. Abstr.*, 1959, 6, 2009). Owing to premature oxidation of I during the titration, it cannot be used in the cerimetric determination of  $U^{IV}$  or  $As^{III}$  but gives good results for quinol or  $Mo^V$ . When determining  $Mo^V$ ,  $H_3PO_4$  should be added to increase the speed of titration. Quinol is titrated in  $N H_2SO_4$  at sufficient dilution to avoid masking of the pink end-point. A 0.1% soln. of I in 3 N acetic acid is stable for 9 months.

P. D. PARR-RICHARD

2600. N-Phenylanthranilic acid as a redox indicator. R. Belcher, D. I. Rees and W. I. Stephen (Dept. of Chem., Univ., Birmingham, England). *Chim. Anal.*, 1959, 41 (10), 397-400.—N-Phenylanthranilic acid (I) shows a transition potential of 0.89 V, and should prove effective for dichromate and ceric titrations. Whilst I is a suitable indicator for the  $Ce^{IV}$ - $Fe^{II}$  titration (acidity  $<4 M$ ) it is not recommended for the titration of  $Fe^{II}$  with  $K_2Cr_2O_7$ , although it may be used for the reverse titration. Low results are obtained when I is used as an indicator in the  $Ce^{IV}$ - $[Fe(CN)_6]^{4-}$  titration. The behaviour of I in these titrations is compared with that of other redox indicators.

J. H. WATON

2601. The visual indication of reductimetric titrations with vanadium(II) sulphate. M. Matrká and Z. Ságner (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1959, 9 (10), 526-527.—The excess of  $VSO_4$  used for the reduction of various organic compounds can be determined with  $(NH_4)_2SO_4 \cdot FeSO_4$  soln., with Safranine T (C.I. Basic Red 2) and neutral red as indicators. Redox indicators with a redox potential  $>-0.1 V$  (e.g., Lauth violet, methylene blue or  $NH_4SCN$ ) cannot be used for the same purpose, as their colour change is influenced by  $V^{III}$  formed during the reaction.

J. ZÝKA

2602. New indicator for the complexometric determination of calcium. D. Goldstein (Min. da Agric., Rio de Janeiro, Brazil). *Anal. Chim. Acta*, 1959, 21 (4), 339-340.—Glyoxal bis-(*o*-hydroxyanil)

(10 ml of a 0.02% ethanolic soln.) is used as indicator in the titration of  $\text{Ca}^{2+}$  (1 to 10 mg in 100 ml of water, 10 ml of  $\text{N NaOH}$  and 1 ml of 0.5% aq. KCN) with 0.01  $M$  EDTA (disodium salt). The colour change is from pink to yellow. Barium and  $\text{Sr}^{2+}$  interfere. H. N. S.

**2603. Contributions to the basic problems of complexometry. I. The blocking of indicators and its elimination.** R. Pfabl (Chem. Inst., Czech. Acad. Sci., Prague). *Talanta*, 1959, **3** (1), 91-94.—The formation of "substitution-stable" complexes from indicators and cations with incomplete inner electron shells, e.g.,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$ , is undesirable in complexometry, and is suppressed by addition of 1:10-phenanthroline (I) as an auxiliary complex-forming agent. Thus Cu (or Co at 50°) can be directly determined, in the presence of I and xylene orange (II), by titration with EDTA. The results agree well with those by other complexometric methods. *Procedure*—To the slightly acid soln. of Cu (>30 mg) add 0.2% aq. II soln. (several drops) and solid hexamine until a red colour appears. Dilute to 200 to 250 ml, add  $10^{-3} M$  I (0.5 ml) and titrate with 0.05  $M$  EDTA to a yellow-green end-point. J. P. STERN

**2604. Complexometric titration of highly coloured ions.** T. S. West (Univ., Birmingham, England). *Chem. Age*, 1959, **82**, 351-352.—The EDTA titration of ions that form highly coloured chelates (e.g., Co and  $\text{Fe}^{3+}$ ) by the use of a fluorescent end-point technique, the thermometric titration of boric acid, and an electrochemical separation process for use in conjunction with polarography for the analysis of certain elements are reviewed. N. E.

**2605. New applications of ion-exchangers in chemical analysis.** J. Inczédy (Gen. Chem. Inst., Polytech. Univ., Budapest). *Magyar Kém. Lapja*, 1959, **14** (10), 409-413.—Recent developments are reviewed, including new preparations, ion-exchange papers and membranes, and redox resins. (49 references.) G. SZABO

**2606. Applications of micro-wave spectroscopy to qualitative and quantitative analysis.** W. Zeil (Inst. Phys. Chem. and Electrochem., Tech. Hochschule, Karlsruhe). *Z. anal. Chem.*, 1959, **170** (1), 19-29.—Micro-wave spectroscopy is used to measure mol. rotation spectra, which are much simpler than vibration spectra. The method is limited to materials with a permanent electric dipole moment and a vapour pressure  $<10^{-3}$  torr at low temp. (solid  $\text{CO}_2$ ). An exception is  $\text{O}_2$ , which has a magnetic dipole yet shows micro-wave absorption. Reflex klystron tubes are used as sources, and cover the range of wavelengths from 10 cm to 5 mm with 10 tubes. Shorter wavelengths can be obtained with frequency multipliers. The absorption cells are 1 to 4 metres long. Silicon diodes are used as detectors. Micro-wave spectroscopy cannot be used to identify atomic groups, but will unambiguously identify a compound from a single line if its spectrum is known. The limit of detection can be as low as  $10^{-11}$  mole, and even lower in the millimetre waveband; the sample can be recovered. Quantitative analyses can be made with a precision of 1%. G. BURGER

**2607. New perspectives in the analytical applications of the Raman effect.** J. Brandmüller (Phys. Inst. der Hochschule, Bamberg). *Z. anal. Chem.*, 1959, **170** (1), 29-43.—Recent advances are reviewed, with 31 references. The topics discussed include

the principles of analysis by means of Raman and resonance Raman spectra, the analysis of mixtures of hydrocarbons and of isomers, the determination of total aromatics and total olefins in oils, the use of added pyridine to give a new line characteristic of the solvent, and the investigation of the structure of unsaturated molecules. G. BURGER

**2608. Fluorescence of crystalline substances and solutions excited by X-rays. Application to analysis.** M. Graulier. *Bull. Soc. Chim. France*, 1959, (10), 1715-1721.—The theory of X-ray fluorescence is reviewed and various experimental arrangements are discussed. The application of X-ray fluorescence as a method of analysis of alloys, minerals, oxide films, catalyst poisons, industrial dust, lead in petrol, metals in aq. soln., and thickness of deposits is reviewed. (60 references.) E. J. H. BIRCH

**2609. Theory of mass spectra.** R. Taubert (St. Wendelstr. 51, Braunschweig). *Z. anal. Chem.*, 1959, **170** (1), 333-348.—An exposition, with 25 references. G. BURGER

See also Abstract—2784, Sulphonic acids as non-aq. titrants.

## 2.—INORGANIC ANALYSIS

*General, determination of elements (arranged in the order of the Periodic Table), analysis of minerals and inorganic industrial products.*

**2610. Determination of gas and water vapour by galvanic micro-piles.** A. Berton. *Bull. Soc. Chim. France*, 1959, (10), 1453-1454.—The micro-piles described consist of pairs of plates of dissimilar metals, separated by a layer of paper, which is irrigated with water, so as to form a cell, the current from which is fed to a galvanometer. With plates of lead and oxidised copper, with water as the irrigating liquid, acid or alkaline vapours can be continuously measured (e.g.,  $\text{SO}_2$  in air can be determined in amounts  $<1$  p.p.m.). Plates of gold and lead, with deliquescent  $\text{P}_2\text{O}_5$  as the separating liquid, can be used to measure water vapour in air in amounts of a few  $\mu\text{g}$  per litre. The lead-lead oxide couple, with conc.  $\text{H}_2\text{SO}_4$  as separating electrolyte, can be used to measure nitrobenzene and pyridine, or, with less sensitivity, saturated and unsaturated hydrocarbons. In this case, the cell must be charged like an accumulator. The possible use of liquid electrodes and of photo-cells is referred to. E. J. H. BIRCH

**2611. Contributions to the extraction of metal carbamates from strong acid solutions.** H. Malissa and S. Gomišek (Max-Planck Inst. für Eisenforsch., Düsseldorf, Germany). *Z. anal. Chem.*, 1959, **169** (6), 401-404.—Distribution coeff. for several metal complexes with Na diethyldithiocarbamate (I) or ammonium tetramethylenedithiocarbamate (II) between their acid soln. and  $\text{CHCl}_3$  have been determined. The results in  $\text{HCl}$ ,  $\text{HClO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and acetic acid are discussed. In 0.1  $N$   $\text{HCl}$ , complexes of Fe, Co, Ni, V, Cu, As, Sb, Sn and Pb with I are quant. extracted by  $\text{CHCl}_3$ ; complexes of Cu, Sb and Sn with II can be quant. extracted even from 6  $N$   $\text{HCl}$ . At pH 3 only Cr, Mn and Cd are incompletely extracted; the best results for most metals are obtained in  $\text{HCl}$  soln. at pH 2 to 3, or in 1  $N$  acetic acid. P. D. FARR-RICHARD



2612. Solvent extraction of metal acetylacetonates. Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Kyoto). *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37** (4), 252-259.—Generally  $\text{CHCl}_3$  is superior to butyl acetate for the extraction of metal acetylacetonates. The extraction of the acetylacetonates of Al, Be,  $\text{Fe}^{\text{III}}$ , Ga, In, Hf and  $\text{UO}_2^{2+}$  is approx. quant., but those of Cd, Co, Mg, Ni and Sr cannot be extracted. Butyl acetate extracts the chelates of  $\text{Fe}^{\text{III}}$ , In and  $\text{UO}_2^{2+}$  quant., but the extraction of chelates of Ce, Cu, Pb, Zn and Mn is not complete. Extraction is not possible in the presence of EDTA except for the chelates of Be and  $\text{UO}_2^{2+}$  which are nearly quant. extracted. *Procedure*—To the sample soln. add 10 ml of 5% aq. acetylacetone soln. and adjust the pH to  $\approx 7$  with  $\text{N NaOH}$  or  $\text{N H}_2\text{SO}_4$ . Dilute to 50 ml with  $\text{H}_2\text{O}$  and extract with 10, 5 and 5 ml of  $\text{CHCl}_3$ .

D. C. ARMSTRONG

2613. Potentiometric studies in oxidation-reduction reactions. Iodimetric determination of reducing substances. S. M. A. Azim and Ahsanul Haq Rehman (Dept. of Chem., Government Coll., Lahore). *Pakistan J. Sci. Res.*, 1959, **11** (4), 143-145.—The potentiometric titration of a number of oxidising and reducing agents is reviewed. The determination of  $\text{HgCl}_2$  (in the presence of KI),  $\text{K}_3\text{Fe}(\text{CN})_6$  (at  $40^\circ$ ),  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{Na}_2\text{S}_2\text{O}_5$  and  $\text{Na}_2\text{S}$  by the addition of a known excess of iodine soln. and potentiometric titration with  $\text{Na}_2\text{S}_2\text{O}_5$  is described, and titration curves are given. Recoveries are  $> 99\%$ .

P. D. PARR-RICHARD

2614. Studies on paper chromatography. II. Separation of lead, bismuth, cadmium, mercury(II) and copper with developers consisting of aqueous solutions of inorganic compounds. Hiromu Imai (Fac. of Engng. Kansai Univ., Oyodo-ku, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1959, **80** (7), 761-763.—The separation of Pb, Bi, Ca, Hg and Cd with one inorg. developer was unsuccessful. An acid sample soln. containing these 5 cations is first developed with 4 N aq.  $\text{NH}_3$ ; Pb and Bi remain at the initial point and Cu, Hg and Cd give  $R_f$  values of  $\approx 0.9$ . The first two are developed with 0.4 N  $\text{H}_2\text{SO}_4$ ; Pb remains at the initial point and Bi gives an  $R_f$  value of  $\approx 0.9$ . The last three are developed with 0.5 N  $\text{K}_2\text{CO}_3$  containing 0.3 M KI; the  $R_f$  values for Cu, Hg and Cd are  $\approx 0.9$ , 0.6 and  $\approx 0$ , respectively.

III. Separation of arsenic, antimony and tin with an inorganic developer. Hiromu Imai. *Ibid.*, 1959, **80** (8), 878-881.—The sulphides of As, Sb and Sn are treated first with  $\text{HCl}$  and  $\text{KClO}_3$  to produce  $\text{As}^{3+}$ ,  $\text{Sb}^{3+}$  and  $\text{Sn}^{2+}$  and then with  $\text{NaNO}_3$  to produce  $\text{Sb}^{3+}$  and  $\text{Sn}^{2+}$ . The product is developed with ammoniacal  $\text{NH}_4\text{HCO}_3$  soln. ( $\approx 1\text{M}$ ); the  $R_f$  values are 0.13, 0.33 and 0.85 for  $\text{Sn}^{2+}$ ,  $\text{Sb}^{3+}$  and  $\text{As}^{3+}$ , respectively. The difference in  $R_f$  values decreases with increase in concn. of the developer.

IV. Separation of iron, aluminium and chromium with an inorganic developer. Hiromu Imai. *Ibid.*, 1959, **80** (12), 1439-1441.—For the separation of these 3 elements, Cr is oxidised to  $\text{CrO}_4^{2-}$ , and the sample soln. is spotted on a filter-paper and kept in a current of  $\text{NH}_3$  for 10 min. When the product is developed with 0.05 to 0.5 N  $\text{NaOH}$ , these elements are separated; e.g., with 0.3 N  $\text{NaOH}$ ,  $R_f$  values are 0, 0.65 and 0.88 for Fe, Al and  $\text{CrO}_4^{2-}$ , respectively. The spots are revealed with oxine in ethanol (Fe, dark brown; Al, light yellow) and Pb acetate.

K. SAITO

2615. Spectrographic determination of hydrogen in metals by isotope equilibration. A. N. Zaidel', A. A. Petrov and K. I. Petrov. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 206-207; *Ref. Zhur., Khim.*, 1959, (19), Abstr. No. 67,682.—In order to eliminate the errors in chemical determinations of H in standards, and the difficulties in their preparation, the method of isotope equilibration is used. The sample (1 to 10 g) is placed in an evacuated and previously de-gassed quartz vessel;  $^3\text{H}$  is introduced under pressure, and, after equilibration (the metal is heated to  $800^\circ$  to  $1100^\circ$ ), the concn. of H to  $^3\text{H}$  is measured spectroscopically. The H content can be calculated from a given formula. In this way H is determined in steel, zirconium, tantalum, zinc, aluminium and certain alloys. The sensitivity of the method depends on the amount of the metal sample and the degree of degasification of the exchange vessel. The coeff. of variation for individual determinations was 3 to 10%.

K. R. C.

2616. Universal apparatus for semi-micro determination of active hydrogen and for quantitative hydrogenation. B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 2948-2953.—An apparatus is described in which the manometric measurement of the gas vol., suggested by Souček (*Ibid.*, 1958, **23**, 554), is improved by incorporating a device for the fine adjustment of the mercury level in the gas burette and a dropping-funnel similar to the dropping-burette of the Soltys apparatus (*Microchem.*, 1936, **20**, 107). The apparatus was tested, with good results, on a semi-micro determination of active hydrogen with Li alanate or with methylmagnesium bromide and on quant. hydrogenation by means of palladium, platinum or Raney nickel.

J. ZÝKA

2617. Determination of denterium, oxygen and nitrogen in helium by gas chromatography. D. L. West (E. I. Du Pont de Nemours & Co., Savannah River Lab., Aiken, S.C.). *U.S. Atomic Energy Comm.*, Rep. DP-392, Sept., 1959. 9 pp.—The precision and accuracy of the gas-chromatographic method were comparable to those of the mass-spectrometric method. The low capital investment, ease of operation and maintenance by non-technical personnel and adaptability to automatic monitoring are the major advantages of this method.

NUCL. SCI. ABSTR.

2618. Absorption measurements using soft X-rays for the determination of argon in synthesis gas. K. Hoffmann and F. Herre (Farbwerke Hoechst A.-G., Frankfurt a.M.-Höchst). *Chem.-Ing.-Tech.*, 1959, **31** (6), 399-401.—The absorption of soft X-rays is used to determine the fraction of high atomic number in simple compounds, with  $^{55}\text{Fe}$  as a radiation source. An absorption tube, 260 mm long, through which passes a stream of synthesis gas, is placed in front of the source. A counter with amplifier, integrator and recorder is used to measure the absorption.

G. P. MITCHELL

2619. Determination of lithium in silicate minerals and leach solutions by flame photometry. H. L. Howling and P. E. Landolt (Arthur D. Little, Inc., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1818-1819.—Minerals are dissolved by treatment with HF and  $\text{HNO}_3$ , followed by fuming with  $\text{H}_2\text{SO}_4$ . This diluted soln., or a leach soln., is treated with solid  $\text{CaCO}_3$  to the methyl red end-point, 10 drops of  $\text{H}_2\text{O}_2$  (3%) are added, and if

necessary more  $\text{CaCO}_3$ , and the mixture is boiled to remove  $\text{CO}_2$ . The soln. is filtered and Li is determined in the filtrate, with a Beckman DU flame spectrophotometer, at 671 m $\mu$ . T. R. ANDREW

2620. Note on the quantitative flame-photometric determination of sodium, potassium and calcium in the presence of large amounts of salts. F. Burriel-Martí, M. L. Rexach-M. de Lizarduy and J. Ramírez-Muñoz (Dept. Quím. Anal., Univ., Madrid, Spain). *Rev. Univ. Ind. Santander, Colombia*, 1959, 1 (1), 37-39.—The method of standard addition is recommended for the determination of up to 4 p.p.m. of K and Na and up to 10 p.p.m. of Ca in solutions containing up to 1% of the salt sample.

G. H. FOXLEY

2621. Indirect radiometric determination of potassium, rubidium and caesium with sodium tetraphenylboron. J. Havří and M. Křivánek (Military Acad., Brno, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, 24 (9), 3183-3185 (in German).—Potassium, Rb and Cs salts react with Na tetraphenylboron (I), the resulting ppt. is dissolved in acetone and the tetraphenylboron component is titrated with  $\text{AgNO}_3$  soln. labelled with  $^{110}\text{Ag}$ . The influence of the acetone content of the soln. to be titrated on the accuracy of the results was studied; the optimum concn. is 33%. Procedure.—To the soln., containing the chloride or sulphate of K, Rb or Cs (1 to 15 mg), add  $\text{HNO}_3$ , adjust the pH to 4 to 5, heat to 60° and add 2% I soln. dropwise. Cool the mixture to room temp., filter off the ppt. and wash it with a satd. soln. of the tetraphenylboron derivative of the element to be determined, and then with a small vol. of  $\text{H}_2\text{O}$ . Dissolve the ppt. in acetone (33 ml), transfer the soln. to a 100-ml flask and add 0.1 N  $\text{AgNO}_3$  (3 to 5 ml) of known activity; dilute to vol. with water, mix and set aside for 5 min. Filter off the pptd. Ag tetraphenylboron on a dry filter; reject the first part of the filtrate, and measure the activity of 10 ml of the remainder with a Geiger-Müller counter. Samples giving 3000 to 5000 counts per min. were used. For 5 to 16 mg of K, Rb or Cs the relative mean errors were  $\pm 0.31\%$ ,  $\pm 1.03\%$  or  $\pm 0.63\%$ , respectively. J. ZÝKA

2622. Low-temperature carbon arc as source for exciting the spectra of rubidium, caesium, thallium and indium in the spectrographic analysis of silicates. A. K. Rusanov, V. G. Khitrov and N. T. Batova (All-Union Inst. of Mineral Raw Materials, Moscow). *Zhur. Anal. Khim.*, 1959, 14 (5), 534-541.—A low-temp. d.c. carbon arc is used for determining these elements in the presence of an excess of K, which lowers the arc temp. and aids fractional evaporation of the elements from the sample. The test material (20 mg of sample or standard mixed with 20 mg of  $\text{K}_2\text{SO}_4$ ) is placed in the cup-shaped lower carbon electrode (anode); the arc gap is 4 to 5 mm, and current 5 amp. The spectra are photographed in a glass spectrograph 3 to 4 sec. after striking the arc, with an exposure of 2 min. The analytical lines and determinable concn. (%) are—Rb 4201-85 or 4215-56 A, 0.002 to 0.2; Cs 4555-36 A, 0.005 to 0.2, or 4593-13 A, 0.05 to 0.5; Tl 3775-72 A, 0.0003 to 0.02 and In 4511-32 or 4101-77 A,  $> 0.02$  (the first cannot be used for Mo-containing minerals, and the second may be covered by lines due to Sn and Ti). Other interfering lines are—for Rb, Fe 4202-03 and Sr 4215-56; for Cs, Ti 4555-49; and for Tl, Ni 3775-57. The mean probable error in determining Rb, Cs, Tl and In is  $\pm 11\%$ . C. D. KOPKIN

2623. Isolation and mass-spectrometric determination of extremely small quantities of alkali. H. Voshage and H. Hintenberger (Max-Planck Inst. f. Chem., Mainz). *Z. anal. Chem.*, 1959, 170 (1), 366-371.—An ion source is described in which minute amounts of alkali salts are completely volatilised by bombardment with electrons and then completely ionised by contact with a hot metal surface. The emitted alkali-metal ions are focused in the mass spectrometer. Amounts of Cs down to  $10^{-12}$  g have been determined with a reproductibility of  $\pm 10\%$ . The metals can be determined directly on mineral samples in this apparatus. The determination of the isotope ratio of K in a meteorite is reported. G. BURGER

2624. New reaction for bivalent copper ions. K. I. Filipova and L. P. Ivanova (Moscow Aviation Technol. Inst.). *Zhur. Anal. Khim.*, 1959, 14 (5), 630.—The method is based on the formation of a dark red ppt. by the reaction of  $\text{Cu}^{2+}$  with *p*-toluidine and  $\text{H}_2\text{O}_2$ . To the test soln. add Na acetate to a pH of 6 to 7, 1 ml of a saturated aq. soln. of *p*-toluidine and 2 drops of a 3%  $\text{H}_2\text{O}_2$  soln. In the presence of Cu a dark red ppt. forms, which is soluble in organic solvents and in acids to form a cherry-red soln. whose colour is stable. The sensitivity in a test-tube is 0.3  $\mu\text{g}$  of Cu per ml, and on a porcelain plate 0.038  $\mu\text{g}$ ; the limiting dilution is 1 in  $4 \times 10^4$ . Other cations do not interfere, except  $\text{Fe}^{2+}$ , which can be oxidised to  $\text{Fe}^{3+}$  with  $\text{HNO}_3$ . Easily hydrolysed cations lower the sensitivity somewhat; in this case a spot test is best used, with 1 drop of each reagent. The reaction has been used to determine Cu in aluminium alloys by the surface-treatment method, with visual colorimetry. Place 1 drop of HCl (1:1) and 2 drops of conc.  $\text{HNO}_3$  on the surface of the alloy freed from oxide, e.g., in a wax cell; after 3 or 5 min. transfer the soln. to a porcelain dish, rinsing the surface with water, add 1 drop each of HCl and  $\text{HNO}_3$ , heat on a water bath and evaporate to dryness. Cool, add a few drops of water, and transfer the soln. to a measuring cylinder. Treat a standard alloy similarly. To each cylinder add 10 drops of a saturated Na acetate soln., 4 drops of a saturated aq. soln. of *p*-toluidine and 2 drops of 3%  $\text{H}_2\text{O}_2$ . After 5 min. add 10 drops of  $\text{H}_2\text{SO}_4$  (1:1). Add water to the more deeply coloured soln. until the colours are equal; the concn. ( $C_1$ ) of Cu in the sample is then  $V_1 C_2 / V_2$ , where  $C_2$  is the concn. of Cu in the standard and  $V_1$  and  $V_2$  are the corresponding volumes. C. D. KOPKIN

2625. Complexometric determination of copper in the presence of amino compounds. W. Bendt and J. Šára (Spolana, Neratovice, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, 24 (9), 3181-3183 (in German).—An excess of EDTA (disodium salt) (I) is added to the sample and the excess is determined with  $\text{ZnSO}_4$  or  $\text{Pb(NO}_3)_2$  soln., with xylenol orange as indicator. The presence of glycerol, asparagine, isoleucine, indol-3-ylacetic acid, *o*-phenylenediamine, diethylamine or ethylenediamine causes no interference. Procedure.—Dilute the soln. (containing  $\approx 10$  mg of Cu) to 200 ml, neutralise with N HCl (dimethyl yellow as indicator), add 0.01 M I (15 ml), adjust to pH 5 with 20% hexamine soln. (10 ml), add 0.1% xylenol orange soln. (5 drops) as indicator and titrate with 0.1 M  $\text{ZnCl}_2$  from yellow-green to red-violet. The mean error is  $\pm 0.3\%$ . J. ZÝKA



**2626. Rapid determination of copper in pyrites and pyrites cinders. I, II.** Shozo Nakao (Nissan Chem. Ind. Ltd., Ooji, Kita-ku, Tokyo). *J. Sulphuric Acid Ass., Japan*, 1959, **12** (7), 185-190; (8), 214-217.—The iodimetric titration was studied in order to decrease the time taken for the determination (10 min.). The dissolution of the sulphide ore in  $\text{HClO}_4$  is complete within 2 min. The effect of Fe is eliminated with  $\text{NH}_4\text{HF}_2$  (7 g per g of Fe). The coeff. of variation is  $\pm 4.7\%$ . **Procedure**—Dissolve 1 g of pyrites ( $< 150 \mu$  particle size) in  $\text{HClO}_4$  (62%) (10 ml), heat to white fumes and make ammoniacal; add 20%  $\text{NH}_4\text{HF}_2$  soln. until the  $\text{Fe}(\text{OH})_3$  dissolves, and 5 ml in excess, and dilute to  $\approx 100$  ml. Add KI soln. (50%) (5 ml) and KSCN soln. (50%) (5 ml) and titrate with  $\text{N Na}_2\text{S}_2\text{O}_8$ , with starch as indicator. Dissolve the cinders (1 g) in conc.  $\text{HCl}$  (5 ml) and heat to white fumes with  $\text{HClO}_4$  (60%) (10 ml), then proceed as before. K. SAITO

**2627. Phase analysis of complex copper ores.** Jen-Yin Yen and Yü-Shan Liu (Dept. of Chem., Peking Univ.). *Acta Chim. Sinica*, 1959, **25** (5), 346-352.—A scheme is outlined for the analysis of copper minerals in admixture, based on separation by extraction with suitable solvents followed by the iodimetric determination of Cu in the extracts. Malachite is extracted from the finely powdered sample (1 to 5 g) with 10% Na K tartrate soln. in 10% NaOH soln. (100 ml) in an atmosphere of N. Cuprite is extracted from the residue with the same tartrate soln. (100 ml), but in an atmosphere of O. The residue is then treated with 2%  $\text{Fe}_2(\text{SO}_4)_3$  soln. in 5%  $\text{H}_2\text{SO}_4$  (100 ml) to dissolve one half of the chalcocite. The residue is extracted with 98% acetic acid (5 ml) and saturated  $\text{Ag}_2\text{SO}_4$  soln. (100 ml) to dissolve bornite and the remainder of the chalcocite. The final residue is treated with conc.  $\text{HCl}$  (10 ml) and conc.  $\text{HNO}_3$  (10 ml) to dissolve the chalcocopyrite. Interference by some foreign minerals is discussed. The results are said to be more reliable than those by the Ageenkov method (cf. *Trudŭ Vses. Konf. Anal. Khim., Izv. Akad. Nauk SSSR*, 1943, **2**, 75). S. H. YUEN

**2628. Measurement of the thicknesses of electrolytic deposits of copper and nickel on a metal base free from these two elements by solution emission spectrography.** J. Boutet and G. Imbert. *Chim. Anal.*, 1959, **41** (10), 389-393.—The electroplated article is coated with Plastisol [a suspension of poly(vinyl chloride)], and a circular window of 10 mm diameter is cut out at the position required. The surface exposed is cleaned with ethyl methyl ketone, and the copper and nickel layers are dissolved by the repeated addition of  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ - $\text{H}_2\text{O}$  (4:1:2). The soln. is withdrawn by means of a capillary, and, together with the rinsings, 50 ml of 22-65%  $\text{Na}_2\text{SO}_4$ -10H $_2\text{O}$  soln., 2 ml of 1% sodium lauryl sulphate and a few drops of conc.  $\text{H}_2\text{SO}_4$ , is diluted to 100 ml. The soln. is placed in the porous cup electrode of a spectrograph, and a u.v. spectrum is taken. For the determination of Cu and Ni, lines at 3274 and 3414 Å respectively, are used, whilst that for Na at 3302.5 Å is used as a standard. Standard soln. containing Cu and Ni are prepared in the same way, with the addition of 25 mg of Fe to allow for any attack on the metal underlying the electrolytic deposits. The spectrographic results agree to within  $\approx 1$  micron with results obtained micrographically. The procedure may be applied to the measurement of electrolytic deposits on metal, or on non-metallic

material, provided that the support contains no Cu or Ni; the thickness may be measured at any point on a surface of any shape, provided that an area of 10 mm in diam. can be delimited. J. H. WATON

**2629. Potentiometric chromatography as a method for detection of trace amounts of silver ions.** J. Machaczka-Janikowa (Dept. Phys. Chem. and Electro-Chem., Jagellonian Univ., Kraków). *Chem. Anal., Warsaw*, 1959, **4** (4), 697-703.—The potentiometric method of Kamiński [Bull. Int. Acad. Polon. Sci., A, 1948, (7-10), 127] was applied to the determination of trace quantities of  $\text{Ag}^+$  eluted with acetic acid from an alumina column. An immediate change of potential of a few hundred mV occurred and was measured on a quadrant electrometer, which was connected with a micro-cell composed of an indicator electrode immersed in the eluate and a reference electrode (antimony). A tin electrode was the most convenient indicator. A number of frontal analyses gave a linear relation between the potential and the logarithm of concn. The concn. of  $\text{Ag}^+$  and the rate of removal from the column by the eluent can be thus established.

L. SMAKOWSKI

**2630. Determination of ultra-micro quantities of silver in platinum sponge by neutron-activation analysis.** D. F. C. Morris and R. A. Killick (Brunel Coll. of Technol., London, England). *Talanta*, 1959, **3** (1), 34-40.—Neutron irradiation for 1 month in BEPO permits the determination of 0.02 p.p.m. of Ag as  $^{107}\text{Ag}$ - $^{109}\text{Ag}$  in platinum sponge (0.3 g) with an accuracy within  $\pm 10\%$ . Higher sensitivity is attainable with larger samples or more intense irradiation. The radiochemical separation of the irradiated Ag on a standardised carrier (1.575% aq.  $\text{AgNO}_3$ ) involves dissolution of the platinum containing the carrier (2 ml) in aqua regia (5 ml), rendering alkaline with aq.  $\text{NH}_3$  soln., and separation of the Ag by pptn. as  $\text{AgCl}$  from  $\text{HNO}_3$ . The Ag is purified by dissolution in aq.  $\text{NH}_3$  soln., treatment with  $\text{Fe}^{III}$  pptn. as  $\text{Ag}_2\text{S}$  from aq.  $\text{NH}_3$  soln., further pptn. as  $\text{AgCl}$ , and finally by electrolysis. The Ag is then converted into  $\text{AgIO}_3$  and counted with a NaI  $\gamma$ -scintillation counter. J. P. STERN

**2631. Polarographic determination of beryllium in a basal solution of tetraethylammonium iodide.** P. N. Kovalenko and O. I. Gelderovich (Rostov-on-Don State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (5), 634-635.—Beryllium can be determined polarographically in a basal soln. of 0.1 M tetraethylammonium iodide at a pH of 2.2 to 2.4, from the reduction wave at  $-1.84$  V. The height of the wave is directly proportional to the concn. of Be. In tests, concn. of Be of from  $0.25 \times 10^{-3}$  M to  $2 \times 10^{-3}$  M have been determined.

C. D. KOPKIN

**2632. Flame photometry by the organic solvent extraction method. I. Determination of magnesium [in aluminium] by the isobutyl methyl ketone extraction of oxinate.** H. Gotō and E. Sudo. *Sci. Rep. Res. Inst. Tohoku Univ.*, 1959, **11** (5), 355-359.—**Procedure**—Dissolve 1 g in 10% NaOH soln. (100 ml), add an iron soln. (1 mg of Fe per ml) (1 ml) to co-precipitate Mg, filter, wash and dissolve the ppt. in  $\text{HCl}$  (1:1) (10 ml). To the soln. add 2% 8-hydroxyquinoline soln. (2 ml), make the soln. alkaline with aq.  $\text{NH}_3$  soln., dilute to 25 ml and extract the magnesium complex with isobutyl methyl ketone (25 ml). Submit the extract to flame photometry (slit width 0.2 mm, wavelength 285.2 m $\mu$ , hydrogen pressure 2.5 p.s.i.

and oxygen pressure 26 p.s.i.). In general, the permissible amounts of other elements is larger than in aq. soln.; as little as 0.01% of Mg can be determined in aluminium by this method as compared with 0.4 to 2% by flame photometry of aq. soln.

K. R. C.

**2633. Use of continuous extraction for the removal of interfering elements in the determination of calcium and magnesium.** J. P. Riley (Univ. of Liverpool, England). *Anal. Chim. Acta*, 1959, **21** (4), 317-323.—Metals that interfere in the titration of Ca and Mg with EDTA are removed before the titration by solvent extraction after conversion into their 8-hydroxyquinoline complexes. Chloroform is used as the solvent in a continuous extractor (*cf. Ibid.*, 1958, **19**, 413), the aq. phase being adjusted to  $\approx$  pH 5.0. The 8-hydroxyquinoline complexes of  $\text{Be}^{2+}$ ,  $\text{Ce}^{3+}$  and  $\text{Cr}^{3+}$  are not extracted under these conditions but, if acetylacetone is also added and the soln. is heated for 30 min. at  $100^\circ$  under reflux, these metals are also removed by the  $\text{CHCl}_3$ . Phosphate,  $\text{AsO}_4^{3-}$  and  $\text{SeO}_4^{2-}$  are pptd. with  $\text{ZrO}(\text{NO}_3)_2$  and the excess of  $\text{Zr}^{4+}$  is subsequently removed in the extraction. Manganese is removed after the extraction by boiling the soln. with  $\text{NaClO}_2$  and filtering off the  $\text{MnO}_2$  that is pptd. The titration of Ca plus Mg ( $> 7.5$  mg) with EDTA is conducted with the use of Eriochrome black T as indicator in a photo-electric titrator, or by visual end-point detection for larger quantities. Calcium is titrated in the presence of NaOH, in screened u.v. light, with calcein as indicator, or the soln. is brought to pH 12.3 with diethylamine and calcon is used as indicator, either visually or in a photo-electric titrator.

H. N. S.

**2634. Radiometric determination of calcium, strontium and magnesium by EDTA titration.** T. Braun, I. Maxim and I. Galateanu (Inst. of Atomic Physics, Bucharest, Romania). *Zhur. Anal. Khim.*, 1959, **14** (5), 542-546.—The indicator is  $\text{AgIO}_3$  labelled with  $^{110}\text{Ag}$ ; the optimum pH for the soln. is from 9.5 to 11.5. Calcium, Sr and Mg in pure soln. are titrated in the presence of the indicator (prepared from irradiated  $\text{AgNO}_3$  and  $\text{KIO}_3$ ) with a soln. of EDTA (disodium salt) (I), and the activity of the soln. above the indicator is measured during the titration; at the end-point it rises sharply because of dissolution of the  $\text{AgIO}_3$ . To determine Ca and Mg when present together, their sum is first determined as described above; KOH is added to a second aliquot to pH 8 to 9, the soln. is heated to between  $60^\circ$  and  $70^\circ$ , a 10% soln. of potassium molybdate is added, the solution is heated to boiling, the pptd.  $\text{CaMoO}_4$  is filtered off and washed with water and 5% ethanol, and Mg is determined in the filtrate; Ca is found by difference. Such direct titrations may be used for ions not hydrolysed at pH 9.5 to 11.5 or which are held in soln. by screening agents (Mg, Sr, Ca, Co, Ni, Cu, Zn, Cd, In, Pb). Elements not held in soln. at this pH, such as Th, Zr, Hg and Bi, may be determined by adding an excess of I at a low pH, adjusting the pH to 9.5 to 11.5, adding the indicator, and back-titrating the excess of I with a soln. of an element whose complex with I is less stable than the complex of the metal being determined; the activity of the soln. is originally high, since the  $\text{AgIO}_3$  is dissolved by I, but falls during the titration and levels off at the end-point. Anions may be determined indirectly by pptn. with a suitable cation; the ppt. is dissolved and titrated with I soln. to determine the cation.

C. D. KOPKIN

**2635. Determination of calcium sulphate in gypsum and [gypsum] plaster by ion-exchange.** R. Pièce (Gips-Union S.A., Bex, Switzerland). *Rev. Matér. Constr. C*, 1959, (524), 107-110.—The sample (0.2 g. ground to  $60\mu$ ) is heated at  $\approx 90^\circ$  for  $\leq 30$  min. with moist Amberlite IR-120 (10 ml) and  $\text{H}_2\text{O}$  ( $\approx 90$  ml), the suspension being stirred and the resin grains crushed at intervals. The mixture is filtered through a disc (porosity G 0) covered with a few ml of fresh resin, and the free  $\text{H}_2\text{SO}_4$  is then titrated with 0.1 N NaOH, with 2:5-dinitrophenol as indicator. The precision and accuracy are claimed to be greater than those of the usual gravimetric method.

W. J. BAKER

**2636. Spectrochemical analysis of the binder films of micro-crystalline layers of zinc sulphide.** L. Vecsernyés and G. Pozsgay (Forsch.-inst. f. Fernmeldetech., Budapest, Hungary). *Acta Chim. Acad. Sci. Hung.*, 1959, **21** (2), 123-129 (in German).—Alkaline-earth metals and silica can be spectrographically determined in the binder films of television screens composed of zinc sulphide-silver phosphor. Calibration curves are prepared from a series of powdered standards. The concn. ranges per g of ZnS are  $10^{-4}$  to  $10^{-8}$  g for Ca, Sr and Ba, and  $10^{-3}$  to  $10^{-1}$  g for  $\text{SiO}_2$ . The results are reproducible to within  $\pm 35\%$  and reasonable agreement was reached with the results obtained by a radioactive isotope dilution method.

G. P. COOK

**2637. Critical examination of the ferrocyanide determination of cadmium and related references.** H. M. Rosenberger and C. J. Shoemaker (Chem. Res. and Engng Dept., A. B. Dick Co., Chicago, Ill., U.S.A.). *Plating*, 1959, **46** (10), 1151-1152.—The titration of Cd soln. with  $\text{K}_4\text{Fe}(\text{CN})_6$  soln., with uranyl acetate as external indicator, gives erroneous results if the  $[\text{Fe}(\text{CN})_6]^{4-}$  soln. is standardised against zinc metal and a calculated conversion factor is used. Potentiometric titration shows that the visual end-point is reached considerably earlier than the true end-point and that good results are obtained only by the compensation of errors. Titration with EDTA is advocated as being free from this disadvantage.

T. R. ANDREW

**2638. Analytical method for the determination of radium in pitchblende ore and barium sulphate concentrates.** U.K.A.E.A. (Production Group, Chem. Services Dept., Springfield, Lancs.). U.K.A.E.A. Rep. PG Report 33 (S), 1960, 17 pp.—The  $\gamma$ -radiation from a sample contained in a sealed aluminium cylinder (10 cm  $\times$  2.5 cm) is measured after 30 days by using a Geiger-Müller counter; the content of Ra is derived from a comparison with the radiation from a standard radium source. Full details are given of the calculations, and of the corrections for self absorption of the radiation and for  $\gamma$ -radiation from  $^{234}\text{Th}$  and  $^{234}\text{Pa}$ . The method was developed at the National Physical Laboratory.

G. J. HUNTER

**2639. Methods for the analysis of aluminium and aluminium alloys. Part 2: Magnesium.** British Standards Institution (2 Park St., London, W.1). B.S. 1728: Part 2: 1952. Amendment No. 1, 18.1.60.—Corrigenda to the method for the determination of calcium are included.

**2640. Studies of analytical methods for trace elements in metals with radioactive isotopes. IV. Determination of aluminium with calcium-45 type cation exchanger.** H. Amano. *Sci. Rep. Res.*

*Inst. Tohoku Univ.*, 1959, **11** (5), 367-374.—The sample soln. containing  $\text{Al}^{3+}$  at pH 3.0 to 4.0 is passed through a column of Ca-R type cation exchanger labelled with  $^{45}\text{Ca}$ . The radioactivity of the eluted Ca is exactly equivalent to the amount of  $\text{Al}^{3+}$  present;  $\text{Mg}^{2+}$  and  $< 5 \text{ mg}$  of  $\text{Fe}^{3+}$  in 30 ml of soln. do not interfere; the concn. of  $\text{NH}_4^+$  must be kept below 3M. By selecting a calcium standard soln. of suitable specific activity, Al can be determined over a range from 0.001 to 10 mg. When the amount of Ca is very small, non-radioactive Ca is added as an isotopic carrier, sufficient to give  $\approx 5 \text{ mg}$  of Ca oxalate dihydrate. Aluminium was determined in carbon steels and the results obtained were in good agreement with those obtained photometrically. K. R. C.

**2641. Chemico-spectrographic analysis of high-purity aluminium.** A. G. Karabash, Sh. I. Pelzulaev, R. L. Silyusareva and V. M. Meshkova. *Zhur. Anal. Khim.*, 1959, **14** (5), 598-602.—Aluminium is pptd. as  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  by means of HCl gas, leaving impurities in soln. Dissolve 5 g of metallic aluminium in 100 ml of 6N HCl and 0.2 ml of 14N  $\text{HNO}_3$ , pass gaseous HCl for 40 min. while cooling in ice, set aside for 20 min. in the cold and pour off the soln. Dissolve the  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in 70 ml of water and repeat the pptn. twice. Combine the soln., and evaporate, finally in a 50-ml quartz dish that has been ignited at  $550^\circ$  and weighed; convert the residue into nitrate by treating three times with 14N  $\text{HNO}_3$ , evaporating each time to a syrupy consistency, ignite to oxides at  $550^\circ$  and weigh. Concentration factors of about 50 to 70 are obtained. The ignited residue is used for the simultaneous spectrographic determination of Be, Mg, Ca, Ba, Ti, V, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Sn, Pb, Sb, Bi and In. The analytical lines and the sensitivity of the determination of these elements are given; the sensitivity is from  $10^{-4}$  to  $10^{-4}\%$ , with a mean relative error of  $\pm 20\%$ . These elements can be determined with a sensitivity of  $10^{-4}$  to  $10^{-4}\%$  without concentration by dissolving a sample of the aluminium in HCl, evaporating three times with  $\text{HNO}_3$ , and igniting to oxides at  $550^\circ$ .

C. D. KOPKIN

**2642. Optical spectrographic determination of aluminium in a titanium alloy.** E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Michigan, U.S.A.). *Appl. Spectroscopy*, 1959, **13** (5), 116-119.—Good reproducibility was obtained in the determination of 6.5% of Al in a titanium alloy by the use of (i) an homologous line-pair close in wavelength, such as Al I 3944.03 and Ti I 3904.78, (ii) argon for flushing the spark gap and (iii) a pre-spark time of 30 sec. to avoid sparking-off effects. A condensed spark source with no added inductance, a 4-mm tandem gap and a 2-mm analytical gap between a massive flat sample piece and a pointed graphite counter-electrode were used throughout the investigation. A coeff. of variation of  $\pm 0.9\%$  was obtained. P. T. BEALE

**2643. Spectrophotometric determination of aluminium and iron with haematoxilin.** L. Guerreschi and R. Romita (Ist. Chim. Anal., Univ., Roma). *Ric. Sci.*, 1959, **29** (10), 2178-2185.—From data already published on the spectrophotometric determination of Al and Fe with haematoxilin (*Ibid.*, 1957, **27**, 3361), empirical correction curves are drawn to enable these metals to be determined simultaneously over the total concn. range 0.1 to  $0.3 \mu\text{g}$  per ml. The extinction of the soln. is measured at 580 and 670 m $\mu$ . J. H. WATON

**2644. Rapid spectrographic determination of aluminium in Nimonic alloy.** O. Bělohlávek (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1959, **14** (9), 809-811.—*Procedure*—Dissolve the comminuted sample (1 g) of Nimonic alloy (which contains 75% of Ni, 20% of Cr, 3% of Ti, 0.5% of Mn, 1% of Al and 0.5% of Fe) in a mixture of HCl (15 ml) and  $\text{HNO}_3$  (10 ml), diluted 1:1; add a soln. of Fe (5 ml  $\equiv$  0.3 g of Fe) as internal standard, dilute to 50 ml and carry out the determination with a rotating carbon electrode, a Q 24 spectrograph and the line-pair Al 3961.53 - Fe 4063.59 Å. The procedure takes  $> 30 \text{ min.}$ , and the accuracy is  $\pm 7\%$ . J. ŽYKA

**2645. Analysis of mixtures of aluminium, gallium and indium oxinates by infra-red spectrography.** R. Neeb (Anorg. Chem. Inst., Univ., Mainz). *Z. anal. Chem.*, 1959, **170** (1), 95-106.—The sum of the metals in a mixture of any two of the elements Al, Ga and In, pptd. by means of 8-hydroxyquinoline, is obtained by weighing the ppt. Their ratio can be determined from the ratio of their characteristic bands in the caesium bromide region of the spectrum of the ppt. (pelleted with KBr). The standard deviation (10 readings) for the same pellet is 0.0046; for different pellets (10 determinations) it is 0.0110. G. BURGER

**2646. Spectrographic determination of aluminium-manganese, aluminium-copper, and aluminium-beryllium alloys.** L. G. Azarova and T. V. Khasina. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 432-434; *Ref. Zhur., Khim.*, 1959, (19), Abstr. No. 67,725.—To determine Mn, Si, Fe and Cu in alloys of aluminium and manganese, and Cu, Si and Fe in alloys of aluminium and copper, spectra were excited in a condensed high-voltage spark discharge from a generator in a simple circuit and registered in a medium quartz spectrograph with a 3-step attenuator attached to the slit. To determine Zn, Fe, Si and Be in alloys of aluminium and beryllium, spectra were excited in the discharge of a low-voltage spark with a capacitance of 20  $\mu\text{F}$ . The results were in good agreement with those obtained by chemical methods. K. R. C.

**2647. Amperometric titration of gallium with EDTA (disodium salt) in the presence of phosphate.** N. N. Chudinova (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 636.—Gallium can be determined in the presence of phosphate by direct amperometric titration with EDTA (disodium salt) (I), by using the anode current for the oxidation of I at a potential of 0.8 to 1.0 V (vs. the S.C.E.), the potential being applied to the electrodes before insertion in the soln. To the soln., containing 1.5 to 40 mg of Ga and 100 to 1000 times this amount of  $\text{PO}_4^{3-}$ , add HCl (1:1) to dissolve the ppt. of  $\text{GaPO}_4$  (pH  $\approx$  1.5 to 2.5), dilute to 25 ml and titrate amperometrically with 0.05M I. The titration curve is L-shaped. The increase in the current at the end-point is proportional to the excess of I up to a concn. of about  $2 \text{ or } 3 \times 10^{-3} \text{ M}$ ; further addition of I has little effect on the current. The error in determining 39.79 to 2.39 mg of Ga varied from 0.027 to 0.42%; in determining 1.59 mg it was 3.1%. C. D. KOPKIN

**2648. Extraction of small quantities of thallium from solutions of non-ferrous metals.** I. V. Tananaev and M. A. Glushkova. *Zhur. Prikl. Khim.*, 1959, **32** (9), 1899-1904.—A method is described for the determination of small amounts of Tl ( $\approx$  0.01 g per litre) in soln. of non-ferrous



metals (Cu, Ni, Co, Cd, Zn) at a total concn. of 0.5 g-ion per litre, based on pptn. with  $\text{Na}_2\text{Fe}(\text{CN})_6$  soln. (1% of that required for the pptn. of all the non-ferrous metals present). After igniting the ppt. at  $700^\circ$  to  $800^\circ$ , Ti is extracted by leaching the ppt. with water. *Procedure*—To the sample soln., containing  $\approx 0.5$  g-ion ( $\approx 30$  to  $40$  g) of non-ferrous metals per litre and 1 to 10 g of  $\text{H}_2\text{SO}_4$  per litre, add the calculated amount of  $\text{Na}_2\text{Fe}(\text{CN})_6$  soln. The copper content of the sample soln. should be less than one-fifth of the total non-ferrous metals present. Mix for 30 min. and filter off the ppt. by decantation; wash it with water and ignite it at  $700^\circ$  to  $800^\circ$  (not lower). Extract the ignited residue with hot water and filter; the filtrate contains all the Ti. Determine Ti by pptn. as chromate.

W. ROUBO

**2649. Quantitative determination of thallium as the dichromate. II. Determination of thallium in the presence of other elements.** N. I. Bashilova and N. I. Solotina (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 556-561.—Univalent Ti is pptd. quantitatively as  $\text{Ti}_2\text{Cr}_2\text{O}_7$  in the cold, with a  $\text{CrO}_3$  soln., from acid soln. containing  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  or  $\text{HClO}_4$ . Elements that do not form sparingly soluble chromates (Zn, Cd, Fe, Cu, Al, Mg, Co, Ni, Sb, In, Ga, Ge and  $\text{Ti}^{III}$ ) do not interfere; in the presence of  $\text{Fe}^{2+}$  a slight excess of  $\text{CrO}_3$  should be used to oxidise Fe to  $\text{Fe}^{3+}$ ; since accurate results are then obtained,  $\text{Cr}^{3+}$  also do not interfere. The allowable concn. of these elements depends only on the solubility of their chromates in the acid soln. Elements that are pptd. by chromate (Pb, Ag, Bi, Hg and Ba) do not interfere unless present in more than a certain limiting concn. For a soln. containing 10% of acid and with 1%  $\text{CrO}_3$  soln., these values are (in 100 ml)— $\text{HgSO}_4$ , 0.05 g;  $\text{Bi}(\text{NO}_3)_3$ , 0.02 g;  $\text{Pb}(\text{NO}_3)_2$ , 0.02 g;  $\text{AgNO}_3$ , 0.01 g; and  $\text{Hg}_2(\text{NO}_3)_2$ , 0.003 g;  $\text{Ba}(\text{NO}_3)_2$  does not interfere. Mixtures of these elements or classes of elements do not interfere provided that the limiting concn. are observed. (For Part I see *Anal. Abstr.*, 1959, **6**, 1226.)

C. D. KOPKIN

**2650. Analytical chemistry of thallium. III. Spectrophotometric determination of thallium with antipyrine [phenazone] derivatives.** A. I. Busev, V. G. Tiptsova and L. M. Afanas'eva (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (5), 550-555.—Diantipyrinylmethane (I) and diantipyrinylbutane (II) precipitate  $\text{Ti}^{III}$  quantitatively from an acid soln. containing KI, the ppt. being  $\text{C}_{28}\text{H}_{24}\text{O}_4\text{N}_4\cdot\text{HTiI}_3$  and  $\text{C}_{32}\text{H}_{28}\text{O}_4\text{N}_4\cdot\text{HTiI}_3$ , respectively. These compounds are soluble in benzene, and the soln. obey Beer's law at 400 to 405  $\mu$ , with molar extinction coeff. of 12,000 in both cases. To determine  $\text{Ti}^{III}$ , to the soln., containing 10 to 200  $\mu$ g of Ti, add 2 to 3 ml of 0.1% KI soln., 1 or 2 ml of 0.05% II soln. or 0.1% I soln. in acetic acid (1:10), and 1 ml of N  $\text{H}_2\text{SO}_4$ ; the total volume should be about 10 ml. Extract with 10 ml of benzene and measure the extinction of the extract at 400 to 405  $\mu$ . The minimum determinable concn. of Ti is 0.3  $\mu$ g per ml. To determine  $\text{Ti}^I$ , first oxidise it with bromine water, boil off the excess of Br, cool, and continue as described above. To determine  $\text{Ti}^{III}$  in the presence of  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$ , add to the soln. a few ml of a 5% soln. of EDTA (disodium salt) soln. (III) and then aq.  $\text{NH}_3$  in slight excess (if a ppt. forms add more III), add the KI and reagent, acidify carefully to pH  $\approx 3$ , preferably with 2 M

acetic acid, extract with benzene and measure the extinction as before. Zinc, In and Ga do not interfere, even in the absence of III. Cadmium does not interfere in concn.  $< 200$  times that of Ti. In the presence of III, Pb does not interfere even in concn. 20,000 times that of Ti. Mercuric ions interfere even in the presence of III. (For Part II see *Anal. Abstr.*, 1960, **7**, 56.)

C. D. KOPKIN

**2651. Complexometric titrations (chelometry). XLIV. Determination of yttrium in mixtures of yttrium earths.** V. Patrovský (Centr. Geol. Inst., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (10), 3305-3308 (in German).—The differences in the atomic weights of Y and other elements of the yttrium group were used for the determination. The Y content is calculated from the equivalents obtained by complexometric titration, with xylenol orange as indicator, and the weight of the sample of mixed oxides. *Procedure for yttrium-earth metals*—Evaporate, almost to dryness, the separated Th-free oxalates of the rare-earth metals with conc.  $\text{HNO}_3$ , dissolve the residue in a small vol. of  $\text{H}_2\text{O}$ , add a satd. soln. of  $\text{K}_2\text{SO}_4$  (5 ml) and solid  $\text{K}_2\text{SO}_4$  (0.5 g) and set aside for 1 hr. in the cold, with occasional shaking. Filter off the ppt. of double sulphates of the cerite-earth metals, dilute the filtrate to 50 ml and precipitate the hydroxides of the yttrium-earth metals with a small excess of aq.  $\text{NH}_3$ . Filter off the ppt., dissolve it in a small vol. of  $\text{HNO}_3$  and repeat the pptn. Wash the ppt. with aq.  $\text{NH}_3$  soln. (2%), dry and ignite to constant weight. Dissolve the ignited and weighed oxides in a small vol. of  $\text{HNO}_3$ , evaporate off the excess of  $\text{HNO}_3$  and dilute with  $\text{H}_2\text{O}$  to 50 to 100 ml. Adjust to pH 5 with Na acetate, acetic acid and hexamine, add a few drops of xylenol orange soln. as indicator, and titrate with 0.02 M EDTA (disodium salt), to a yellow end-point.

J. ŽYKA

**2652. Separation of rare-earth metals by means of anion exchange.** R. Dyczyński (Dept. of Anal. Chem., Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1959, **4** (3), 531-534.—It was found that the rare-earth metals can be adsorbed on a strongly-alkaline anion-exchange resin and that lanthanide elements adsorbed on an Amberlite IRA-400 (EDTA form) column can be desorbed by lowering the pH of the soln. By means of radioactive tracers it was shown that the stabilities of the EDTA-lanthanide complexes permits their separation by column chromatography. The separation of traces of lighter lanthanide elements was accomplished, and it was noted that the sequence of elution was reversed as compared with that of the same elements when a cation-exchange resin was used.

W. B. MIASKOWSKI

**2653. Complete spectrographic analysis of mixtures of rare-earth-metal oxides.** R. R. Shvangiradze. *Zhur. Anal. Khim.*, 1959, **14** (5), 562-566.—Mixtures of rare-earth-metal oxides are analysed by using Ce, Nd, Sm or Y as comparison element. Calibration curves are constructed from standard samples containing the comparison element and the elements to be determined, on the co-ordinates  $\log I_{\alpha_i}/I_A$  vs.  $\log \alpha_i$ , where  $I_{\alpha_i}$  and  $I_A$  are the intensities of the lines of the element to be determined and of the comparison element, and  $\alpha_i$  is the ratio (%) of the concn. of the element  $x_i$  to the concn. of the comparison element A. For the samples, the value of  $\alpha_i$  is found from the graph, the concn.  $C_A$  of A is found from the equation  $C_A = 10^{4\alpha_i}$

( $100 + \Sigma a_i$ ), and the concn. of each component  $x_i$  is found from the equation  $C_{a_i} = a_i C_A / 100$ . Tables give the analytical line pairs for determining the rare-earth-metal oxides with Ce, Nd, Sm and Y as comparison elements, and the concn. range which may be determined in each case. With Sm as comparison element, the mean arithmetical error is  $\pm 7$  to  $8\%$ ; with the others it is  $\pm 2$  to  $4\%$ .

C. D. KOPKIN

**2654. Chromatographic procedure for the determination of rare-earth metals, particularly cerium-earth metals.** G. Brunisholz and J. P. Quinche (École de Chim., Lausanne). *Chimia*, 1959, **13** (10), 331.—The mixture of rare-earth metals is separated on a column of Dowex 50WX2 ( $H^+/Cu^{++}$  form). The eluent is a  $0.04 M$  soln. of the ammonium salt of EDTA buffered to pH 4.6 with ammonium acetate, and the elution rate is 4 ml per day. After 2 or 3 days the zones of the separated elements are detected and measured under u.v. illumination. The concn. of each element is calculated from the length of its zone; La, Ce, Pr, Nd, Sm, Eu, Dy, Ho and Er can be determined, but not Gd, Tb, Y, Tm, Yb or Lu.

W. T. CARTER

**2655. Spectrophotometric determination of quadri-valent cerium with strychnidine.** V. Voicu and I. Dema (Inst. Atom. Phys., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (3), 423-430.—The method is based on the oxidation of strychnidine by  $Ce^{4+}$  in an acid medium with formation of an intensely red acid derivative. The use of acetic acid instead of  $H_2SO_4$  is recommended to prevent interference by  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Sc^{3+}$ ,  $Ti^{4+}$ ,  $VO_3^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $PO_4^{3-}$  and  $SiO_2$ . *Procedure*—A soln. of  $Ce(SO_4)_2$  in conc.  $H_2SO_4$  (containing  $< 16 \mu g$  of Ce per ml) is treated with 1 ml of an acetic acid soln. of strychnidine (0.1%) and made up to 50 ml. The extinction is measured in a Pulfrich spectrophotometer at  $496 m\mu$  against a reagent blank. From 3.2 to  $18.2 \mu g$  of  $Ce^{4+}$  per ml can be determined. The following ions, in concn. of 1 in 2000, do not interfere— $NO_3^-$ ,  $Zr^{4+}$ ,  $Th^{4+}$  and  $U^{4+}$ ; nor do  $La^{3+}$  (1 in 2500);  $Fe^{3+}$  (1 in 4000) do not interfere if masked by 0.1 ml of conc.  $H_3PO_4$ ;  $Sc^{3+}$ ,  $Y^{3+}$ ,  $In^{3+}$ ,  $Ga^{3+}$ ,  $PO_4^{3-}$  and  $Ce^{3+}$  do not give the colour reaction;  $Be^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $S_2O_8^{2-}$ ,  $Ti^{4+}$ ,  $VO_3^-$ ,  $MnO_4^-$ ,  $CrO_4^{2-}$  and  $Cr_2O_7^{2-}$  interfere. H. SHER

**2656. Determination of cerium(III) oxalate.** A. Glasner and M. Steinberg (Dept. of Inorg. and Anal. Chem., Hebrew University, Jerusalem, Israel). *Anal. Chem.*, 1959, **31** (11), 1922.—The titration of  $Ce^{III}$  oxalate with permanganate gives high results because of the partial oxidation of  $Ce^{III}$  to  $Ce^{IV}$ . In order to determine the composition of the  $Ce^{III}$  oxalate, the pptd. oxalate was collected in a sintered glass filter, and washed with water (until there was no reaction for oxalate), 95% ethanol and ether. A weighed portion was transferred to a porcelain basin and digested with NaOH soln. (15%); the  $Ce(OH)_3$  was filtered off, ignited to  $Ce_2O_3$  and weighed; the oxalate was determined in the filtrate with  $KMnO_4$  in the usual manner. The composition was calculated as  $Ce_2(C_2O_4)_3 \cdot 8.5H_2O$ .

T. R. ANDREW

**2657. The routine counting of carbon-14.** M. Peisach (Nat. Chem. Res. Lab., S. Afr. Council for Sci. and Ind. Res., Pretoria, S. Africa). *J. S. Afr. Chem. Inst.*, 1959, **12**, 57-61.—In the method described, a suspension of the barium carbonate to be counted is centrifuged on to a metal planchet

held in the bucket illustrated. This produces a thin uniform deposit over a large area.

E. G. CUMMINS

**2658. Independent titration of cyanide and sulphide.** M. Wroński (Dept. of Chem. Technol., Univ. of Łódź, Poland). *Analyst*, 1959, **84**, 668.—For sulphide, the sample is titrated with 0.03 N o-hydroxymercuribenzoic acid (I), in the presence of formaldehyde, NaOH and dithizone, until the yellow colour changes to purple. For cyanide, the sample soln. is treated with  $NH_4Cl$  and aq.  $NH_3$ , a controlled excess of I (to complex the sulphide) and murexide soln., and is then titrated with 0.1 N  $NiSO_4$  until the colour changes from red to yellow. There is no interference from  $SO_3^{2-}$ ,  $S_2O_3^{2-}$  or  $SCN^-$  in either titration. For the argentimetric titration of  $CN^-$ , the sample soln. is treated with NaOH soln. and a soln. of thiofluorescein in dil. aq.  $NH_3$ , and is then titrated with 0.1 N  $AgNO_3$  until the blue colour changes sharply to a green tinge. Halogens and  $Zn^{2+}$  do not interfere. A. O. JONES

**2659. Spectrophotometric determination of silicon in materials decomposed by hydrofluoric acid. I. Loss of silicon by decomposition with hydrofluoric acid.** F. J. Langmyhr and P. R. Graff (Univ. of Oslo, Blindern, Norway). *Anal. Chim. Acta*, 1959, **21** (4), 334-339.—It is shown experimentally that no loss of Si occurs by volatilisation or otherwise when  $SiO_2$  in milligram quantities is dissolved in 5 ml of conc. HF (35 to 40%). When soln. of  $SiO_2$  (50 mg) in conc. HF (5 to 20 ml) are evaporated at  $\approx 21^\circ$ ,  $60^\circ$  and  $100^\circ$ , respectively, no appreciable loss of Si occurs until the wt. of the soln. is reduced to 2 to 4 g.

H. N. S.

**2660. The improvement of the photometric determination of silicon.** Z. Konečný (VTŽ Chomutov, Czechoslovakia). *Hutn. Listy*, 1959, **14** (10), 903-905.—*Procedure*—Dissolve the sample (0.25 g) in an acid mixture (72 ml of conc.  $H_2SO_4$  and 91 ml of  $HNO_3$  diluted to 1 litre with  $H_2O$ ) (25 ml) by heating, remove the nitrogen oxides, cool and dilute to 250 ml. To 20 ml of this soln. add ammonium molybdate soln. (2.5%) (10 ml) and, after 10 min. (exactly), oxalic acid soln. (5%) (10 ml),  $(NH_4)_2SO_4 \cdot FeSO_4$  soln. (6 g with 1 ml of 3.5%  $H_2SO_4$  diluted to 1 litre) (5 ml), and dilute with  $H_2O$  to 100 ml; measure the extinction with a Pulfrich photometer with a S61 filter. Compare with a calibration curve. The time required is 20 min. The accuracy is within  $\pm 0.02\%$  of Si.

J. ZÝKA

**2661. Volumetric determination of silica.** J. Louvrier and I. A. Voinovitch (Lab. de Chim., Soc. Franç. de Céram., Paris). *Ind. Céram.*, 1959, (510), 243-247.—The procedure given is a slight modification of Sajo's method (cf. *Anal. Abstr.*, 1956, **3**, 732); the Si is pptd. quant. at  $\approx 25^\circ$  as  $K_2SiF_6$  in strongly acid soln. satd. with KCl containing a few ml of 20% aq.  $CaCl_2$  soln. to avoid interference by Al. The ppt. is collected, washed with a satd. soln. of KCl in 50% ethanol, and then hydrolysed with  $H_2O$  at  $70^\circ$  to  $90^\circ$ . The liberated HF is then titrated with 0.05 N NaOH, with a mixed indicator (0.5% bromothymol blue-0.5% phenol red). A reagent blank is run concurrently; the accuracy is often higher than that of the standard gravimetric method, and the max. deviation from the mean is  $\pm 0.80$  (11 analyses of burnt clay). The method is rapid ( $\approx 2$  hr.), adaptable to the use of the automatic titrator, and obviates initial separations (even when 17



different elements are present). In addition to the materials listed by Sajo, the following have been successfully analysed for  $\text{SiO}_2$ —kaolin, clay, chamotte, bricks, burnt ceramic pastes, feldspar, frits and glazes (containing V, Mn, Pb, Ba, Sn, Sb, Zn, Zr and B).  
W. J. BAKER

**2662. The enrichment of very small amounts of silica by ion exchange.** R. Wickbold (Chem. Werke, Hüls A.-G., Marl, Recklinghausen, Germany). *Z. anal. Chem.*, 1959, **171** (2), 81-87.—An enrichment procedure is described whereby the silica content of commercial de-ionised water may be determined. The sample of water, containing 7.5 g per litre of  $N$  HF, is passed down a strongly basic ion-exchange column (e.g., Permutit ES), which adsorbs the silica as  $\text{SiF}_6^{4-}$ . The silica is recovered by washing the column with boric acid (satd. aq. soln.), and the silica in this eluate is determined by the usual colorimetric procedure. All soln. must be freed from traces of silica, as must the water used to prepare the soln., and all soln. must be stored in polyethylene containers. The column is made up of Perspex.  
H. M.

**2663. Slopes of working curves in emission-spectrometric analysis of certain silicates.** J. K. Hurwitz (Appl. Res. Lab., U.S. Steel Corp., Monroeville, Pennsylvania, U.S.). *Appl. Spectroscopy*, 1959, **13** (5), 113-116.—Large deviations from unity of the slopes of working curves have been attributed by Strock (*Ibid.*, 1953, **7**, 64; 1954, **8**, 105) to collisions of the second kind occurring in the d.c. arc discharge, when analysing pseudo-wollastonite, diopside and anorthite. In a series of experiments on these materials it is shown, by a statistical treatment of the results, that deviations from unity are explained by the relatively large errors inherent in the method or by self-absorption.  
P. T. BEALE

**2664. Spectrophotometric determination of germanium with 1:1'-dianthrimide.** O. B. Skaar and F. J. Langmyhr (Univ. of Oslo, Blindern, Norway). *Anal. Chim. Acta*, 1959, **21** (4), 370-374.—When soln. of  $\text{GeO}_2$  (0.2 to 1.0 mg of Ge) in dil. aq. NaOH soln. are heated with a soln. of 1:1'-dianthrimide in conc.  $\text{H}_2\text{SO}_4$  a coloured complex is formed with an absorption max. at 660 m $\mu$ . Equilibrium is reached in 16 hr. at 70° and the concn. of  $\text{H}_2\text{SO}_4$  is critical. Borate ions interfere.  
H. N. S.

**2665. Determination of germanium in ammonia liquor.** J. Gottfried and V. Jára (Res. Inst. Inorg. Chem., Ústí Nad Labem, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (9), 471-472.—A method based on the decomposition of the sample with bromine in an alkaline medium has been developed. The Ge ( $10^{-4}$  to  $10^{-3}$  g per litre) is extracted with  $\text{CCl}_4$  from a HCl medium. *Procedure*—To the sample (50 ml) add NaOH soln. (20%) (3 ml) and bromine (3 ml), and heat for 20 to 30 min. on a sand bath till clear. Cool and acidify with formic acid, with shaking, till the brown colour is discharged. Transfer the soln. to a separating-funnel, add  $\text{CCl}_4$  (50 ml) and conc. HCl (215 ml) and shake, with cooling, for 3 to 4 min.; repeat the extraction with 30 ml of  $\text{CCl}_4$ . Combine the  $\text{CCl}_4$  extracts and wash with a few ml of 9  $N$  HCl. Separate the  $\text{CCl}_4$  layer and shake it twice for 5 min. with  $\text{H}_2\text{O}$  (12 ml and 8 ml). Transfer the aq. layers to a 50-ml flask, add HCl (1:1) (10 ml), gum acacia soln. (5 ml) and phenylfluorone soln. (0.03% ethanolic) (15 ml), and after 30 min. determine the Ge content photometrically. The method cannot

be used for all kinds of ammonia liquor since, in samples with a high phenol and naphthalene content, bromine derivatives are pptd.; these contain no Ge, but interfere with the separation of the solvent layers during extraction. J. ZYKA

**2666. Amperometric determination of tin with cupferron.** S. S. Yamamura, J. E. Rein and G. L. Booman (Atomic Energy Division, Phillips Petroleum Co., Idaho Falls, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1868-1870.—See *U.S. Atomic Energy Comm.*, Rep. IDO-14436; *Anal. Abstr.*, 1959, **6**, 878.  
T. R. ANDREW

**2667. Photometric determination of tin in copper-base and lead-base alloys.** C. L. Luke (Bell Telephone Lab., Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1803-1804.—A photometric procedure, in which phenylfluorone is used, is proposed for the determination, at 510 m $\mu$ , of 0.1 to 25% of Sn in copper- or lead-base alloys. No separations are necessary. A suitable concn. range is from 0 to 50  $\mu\text{g}$  of Sn and not more than 100  $\mu\text{g}$  of Bi, 50  $\mu\text{g}$  of Ti, 100  $\mu\text{g}$  of Fe or 100  $\mu\text{g}$  of Sb can be tolerated. Good results have been obtained on most of the standards tested.  
T. R. ANDREW

**2668. Complexometric titrations (chelatorimetry). XLIII. Masking of some bivalent metals with 1:10-phenanthroline. Selective determination of lead and aluminium.** R. Přibil and F. Vydra (Anal. Lab., Inst. Phys. Chem., Acad. Sci., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 3103-3107 (in German).—In weakly acid soln. (pH 5 to 6, hexamine buffer), 1:10-phenanthroline (I) forms stronger complexes with Cd, Zn, Co, Ni and Mn than does EDTA (disodium salt) (II). Tervalent metals, rare-earth metals and  $\text{Pb}^{2+}$  do not react with I. This is the basis of a highly selective determination of Pb, and an indirect determination of Al. (i) *Procedure for Pb alone*—To a slightly acid soln. of  $\text{Pb}^{2+}$  add an excess of 0.15  $M$  I (pH 5 to 6) and a few drops of xylenol orange soln. (III). Then add solid hexamine (IV) till a red-violet colour appears, and titrate with 0.05  $M$  II to a yellow end-point (green if Cu is present); Pb (47.5 mg) can be determined in the presence of Cu, Ni, Co and Zn (3 to 30 mg), Cd (5 to 50 mg) and Mn (3 to 15 mg) with a mean relative error of  $\pm 0.25\%$ . (ii) *Pb and Cd (or Zn)*—The two metals are titrated together, in the soln. buffered with IV, with II soln., with III as indicator;  $\text{Pb}(\text{NO}_3)_2$  soln. (1 to 2 drops) is added, followed by I soln. in small portions, and after 1 min. the liberated II (corresponding to the Cd or Zn) is titrated with  $\text{Pb}(\text{NO}_3)_2$  soln. The end-point is reached when the red-violet colour of the soln. remains constant on the addition of I. (iii) *Pb and Ni (Co or Cu)*—Since Ni, Co and Cu form strong complexes with III, an excess of II is added, the pH is adjusted with IV (indicator paper) and the excess of II is back-titrated with 0.05  $M$   $\text{Pb}(\text{NO}_3)_2$ . This gives the sum of the two metals; the procedure is then as described in (ii). (iv) *Bi, Pb and Zn (or Cd)*—The soln. is acidified to pH 2 to 3 with  $\text{HNO}_3$ , and the Bi is titrated with II soln., with III as indicator;  $N$  NaOH is then added till a red-violet colour appears, followed by a few drops of  $N$   $\text{HNO}_3$ , and IV till the red-violet colour re-appears. The procedure thereafter is as described in (ii). (v) *Determination of Al*—An excess of II is added to a weakly acid soln. of  $\text{Al}^{3+}$ ; the soln. is boiled for 2 min., diluted to 100 to 150 ml and cooled. Then III is added, followed by IV until the soln. becomes pale orange; sufficient 0.15  $M$  I is then

added to mask the bivalent cations, and the excess of II is back-titrated with 0.05 M  $\text{Pb}(\text{NO}_3)_2$ ; Al (14.2 mg) can be determined in the presence of Zn, Co, Ni and Mn (3 to 15 mg), Cu (3 to 30 mg) and Cd (2 to 25 mg) with a mean relative error of  $\pm 0.14\%$ . J. ZYKA

**2669. Spectrographic determination of copper, tin, antimony, bismuth and silver in antimonial lead.** T. Ya. Kochergina and V. A. Zaitseva. *Fiz. Sb. L'vov. Univ.*, 1958, [4 (9)], 438-439; *Ref. Zhur.*, *Khim.*, 1959, (19), Abstr. No. 67,732.—Samples and standards were in the form of rods (6 mm in diam.) with wedge-shaped ends. Spectra were excited in a low-voltage spark discharge with 4  $\mu\text{F}$  capacitance and 8-amp. current. The generator, provided with a breaker working at 150 sparks per min., operated on a 3-mm spark gap. The spectra were photographed with a medium spectrograph with a 25- $\mu$  slit-width. The results of spectrographic and chemical determinations were in good agreement. Determinations were carried out with the use of the following lines in  $\text{A}$  (figures in brackets indicate concn. range in %): Cu 3274 (0.006 to 2.9), Sn 3175 (0.13 to 1.8), Sb 3232 (0.3 to 10), Bi 3067 (0.012 to 8), Ag 3280 (0.003 to 0.024); the comparison line was Pb 3220. K. R. C.

**2670. Polarographic determination of titanium in tantalum and niobium concentrates and ores.** Dilip K. Banerjee, C. C. Budke and F. D. Miller (Res. Div., U.S. Industrial Chemicals Co., Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (11), 1836-1839.—Titanium gives a polarographic wave at  $E_1 = -0.35 \text{ V}$  vs. the S.C.E. in a supporting electrolyte 5.4 M in  $\text{H}_2\text{SO}_4$  and 0.2 M in  $\text{K}_2\text{S}_2\text{O}_8$ . The sample (0.1 to 0.15 g) is fused with  $\text{K}_2\text{S}_2\text{O}_8$  (5 g) in a platinum crucible and the cooled melt is extracted with  $\text{H}_2\text{SO}_4$  (5 to 10 ml). The soln. is transferred to a 100-ml flask containing  $\text{H}_2\text{O}$  (20 ml), sufficient  $\text{H}_2\text{SO}_4$  is added to give a total acid vol. of 30 ml, and the soln. is diluted to volume with water, and examined polarographically. Tantalum, Nb, Fe, Sn, Mn and W do not interfere, V enhances the Ti diffusion current and Mo interferes. Good results are reported for from 0.25 to 5.0 mg of Ti.

T. R. ANDREW

**2671. 2-Mercaptoacetic (thioglycolic) acid as a reagent for zirconium.** Suseela B. Sant and Bharat R. Sant (Carr Lab., Mt. Holyoke Coll., S. Hadley, Mass., U.S.A.). *Talanta*, 1959, **3** (1), 95-96.—Thioglycolic acid (I) precipitates Zr quant. at pH 4.5; a basic salt is formed which is ignited and weighed as  $\text{ZrO}_2$ . Alkaline- and rare-earth metals, Mn, Mg, Be, Al,  $\text{Ce}^{III}$ ,  $\text{Cr}^{III}$ ,  $\text{Fe}^{III}$ ,  $\text{VO}^{2+}$  and  $\text{UO}_2^{2+}$  do not interfere, but  $\text{Sn}^{II}$ ,  $\text{Hg}^{II}$ , Zn, Cd,  $\text{Ti}^{IV}$ , Th, Cu, Pb, Ni, Co and Bi are co-precipitated. Results on 17 to 220 mg of  $\text{ZrO}_2$  agree to within  $\pm 0.1\%$  with those by the m-nitrobenzoic acid method. *Procedure*—Dilute the  $\text{Zr}(\text{NO}_3)_2$  soln. to  $\approx 150 \text{ ml}$ , add 5% I soln. (10 to 15 ml) and methyl orange indicator, and then set aside at  $85^\circ$  to  $90^\circ$  for 15 min. and filter after 1 hr. Wash with 5%  $\text{NH}_4\text{NO}_3$  soln., dry, ignite and weigh as  $\text{ZrO}_2$ . J. P. STERN

**2672. Determination of zirconium with N-benzoyl-N-phenylhydroxylamine.** I. P. Alimarin and Yun'-Syan Tsze (M. V. Lomonosov Moscow State Univ.). *Zhur. Anal. Khim.*, 1959, **14** (5), 574-577.—N-Benzoyl-N-phenylhydroxylamine (I) precipitates Zr from acid soln. as  $\text{ZrI}_2$ , a white easily coagulating ppt. which may be weighed as such or ignited to  $\text{ZrO}_2$ . Pptn. is shown to be complete in 2-4 N

$\text{HCl}$  and 3-6 N  $\text{H}_2\text{SO}_4$ , in the presence or absence of tartaric acid or  $\text{H}_2\text{O}_2$ . *Procedure*—To the acid soln. add an excess (0.4 to 0.5 g) of I dissolved in 100 ml of boiling water, heat on a boiling-water bath for 15 to 20 min., with occasional stirring, filter hot, wash the ppt. with 1%  $\text{HCl}$  containing 0.05% of I, dry it and ignite to  $\text{ZrO}_2$  at  $1000^\circ$  to  $1100^\circ$ . Iron, Al, Ti, Cr, Nb, Ta and rare-earth metals do not interfere. In determining 0.0016 to 0.0303 g of pure zirconium, and 0.0031 g of Zr in the presence of the indicated elements, the maximum error was  $\pm 0.0002 \text{ g}$ . C. D. KOPKIN

**2673. The analytical chemistry of zirconium. V. Solochrome violet R as a reagent for the spectrophotometric determination of microgram quantities of zirconium.** J. Korkisch and M. Osman (Chem. Inst., Univ. Vienna, Austria). *Z. anal. Chem.*, 1959, **171** (2), 107-111.—Amounts of Zr between 0.1 and 2.0  $\mu\text{g}$  per ml can be determined colorimetrically with Solochrome violet R (C.I. Mordant Violet 5) (I). The Zr soln. (preferably from an ion-exchange separation) is ignited in a platinum dish and taken up in HF. The excess of acid is evaporated on a water bath and the residue is dissolved by warming in  $>7 \text{ ml}$  of 0.1 N  $\text{HCl}$ . The soln. is transferred to a 10-ml flask and 1 ml of reagent (0.01% aq. soln. of I) and 1 ml of Th soln. (0.1 N  $\text{HCl}$  soln. of  $\text{ThCl}_4$  containing 1 mg of Th per ml) are added. The soln. is made up to 10 ml. The red-violet colour is measured at 560 m $\mu$  and the absorption is compared with a calibration curve prepared with a standard soln. of Zr. For amounts of Zr between 0.1 and 1.0  $\mu\text{g}$  the accuracy is  $\pm 7\%$ , while for amounts between 1.0 and 2.0  $\mu\text{g}$  the accuracy is  $\pm 4\%$ . H. M.

**2674. Spectrophotometric determination of zirconium with 1:8-dihydroxy-2:1'-azonaphthalene-3:6:4'-trisulphonic acid.** Sachindra Kumar Datta (Darjeeling Gov. Coll., Calcutta). *Z. anorg. Chem.*, 1959, **301**, 215-219.—Zirconium forms a reddish-brown complex with this compound, which makes it possible to determine the Zr spectrophotometrically. Several ions interfere with the determination.

NUCL. SCI. ABSTR.

**2675. Zirconium analysis by production control Quantometer.** C. L. Easterday (Mallory-Sharon Metals Corp., Ashtabula, Ohio). *Anal. Chem.*, 1959, **31** (11), 1867-1868.—The principles of point-to-plane analysis with a Quantometer are described. Results obtained are comparable with carrier-distillation techniques and photographic recording.

T. R. ANDREW

**2676. Study of the co-precipitation of zirconium with cerium(III) oxalate by homogeneous precipitation.** V. P. Shvedov, N. A. Pavlova and M. I. Bulatov (Lensoviet Leningrad Technol. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (5), 571-573.—The radioactive isotopes  $^{90}\text{Zr}$  and  $^{144}\text{Ce}$  were used in this investigation. With 25 ml of a soln., 0.15 N in  $\text{HNO}_3$ , containing 13.2 g of Ce (as nitrate) per litre and about  $10^{-11} \text{ g}$  of Zr per litre, and pptn. at  $30^\circ$  with four times the theoretical amount of dimethyl oxalate, the pptd. Ce oxalate contained 56.1% of the Zr; after one re-crystallisation it contained 18.5%, and after two re-crystallisations about 7% of the Zr. Increasing the concn. of  $\text{HNO}_3$  increases the solubility of Ce oxalate and causes decreased co-pptn. of Zr. Increasing the concn. of Zr increases the amount pptd., but the percentage of the Zr adsorbed is reduced. C. D. KOPKIN

2677. Analytical applications of xylenol orange. III. Spectrophotometric study of the hafnium-xylenol orange complex. K. L. Cheng (Kelsey-Hayes Co., New Hartford, N.Y., U.S.A.). *Talanta*, 1959, 3 (1), 81-90.—The complex of Hf with xylenol orange (I) is very similar to the Zr-I complex (cf. *Anal. Abstr.*, 1959, 6, 2916, 4716), but the mol. extinction at the max. (540 m $\mu$ ) is 48,700 in 0.3 N HClO<sub>4</sub> and varies greatly with HClO<sub>4</sub> concn. Thus I is suitable for the determination of Hf in 0.3 to 0.8 N HClO<sub>4</sub>, the interference of Fe and Bi being suppressed by hydroxyammonium chloride and that of Zr by H<sub>2</sub>O<sub>2</sub>. Oxalate, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup> and SO<sub>3</sub><sup>2-</sup> inhibit colour formation, but interference by F<sup>-</sup> can be obviated by the addition of Be. The accuracy is  $\approx \pm 10\%$  on 17 to 70  $\mu$ g of Hf in the presence of 17 to 100  $\mu$ g of Zr.

J. P. STERN

2678. Studies of analytical methods for trace elements in metals by using radioactive isotopes. V. Determination of hafnium in zirconium by the isotope dilution method. H. Amano. *Sci. Rep. Res. Inst. Tohoku Univ.*, 1959, 11 (5), 383-392.—The Hf content of zirconium metal was determined by using the isotope dilution method combined with extraction by an organic solvent. A small amount of Hf in a large amount of zirconium was concentrated by four successive extractions with NH<sub>4</sub>SCN-isobutyl methyl ketone and stripping with HCl. Pure Hf was then obtained by passing the acid soln. through an acid-type cation-exchange column and eluting with a mixture of 0.45 M HNO<sub>3</sub> and 0.095 M citric acid. For the calculation of the specific activity, the amount of Hf was determined colorimetrically. The plot of the reciprocal of specific activity vs. the concn. of Hf showed a good linear relationship;  $< 0.025\%$  of Hf in zirconium could be detected by this method.

K. R. C.

2679. Potentiometric titration of thorium ions with potassium ferrocyanide. A. Basinski and M. Langó (Dept. Phys. Chem., Toruń Univ.). *Chem. Anal.*, Warsaw, 1959, 4 (4), 691-697.—Potentiometric titration of thorium with potassium ferrocyanide gives reproducible and accurate results.

L. SMAKOWSKI

2680. Analytical chemistry of thorium. I. Complexometric determination of thorium in monazite concentrates. Yu. A. Chernikhov, V. F. Luk'yanov and A. B. Kozlova. *Zhur. Anal. Khim.*, 1959, 14 (5), 567-570.—Decompose the sample (20 g) with H<sub>2</sub>SO<sub>4</sub> in the normal way, extract the sulphates with ice water (500 to 700 ml), transfer the unfiltered soln. to a 1-litre flask, allow the soln. to reach room temp. and make up to vol. Filter a portion of the soln. and to 50 ml add 140 ml of a potassium (or sodium) metaperiodate soln. containing 10 g of KIO<sub>4</sub>, 40 ml of conc. HNO<sub>3</sub> and 100 ml of water, add, while stirring, 50 ml of a 12% sucrose soln. (in two portions with a 30-min. interval), filter off the ppt., and wash it 6 or 7 times with a hot soln. containing 8 g of KIO<sub>4</sub>, 100 ml of conc. HNO<sub>3</sub> and 900 ml of water. Dissolve the ppt. on the filter in HCl (1:1) containing Na<sub>2</sub>SO<sub>4</sub>, wash the filter several times with water (the vol. should not exceed 75 to 100 ml), and add solid Na<sub>2</sub>SO<sub>4</sub> to the soln. till it is colourless. Neutralise with aq. NH<sub>3</sub> (1:1) to a slight turbidity, and add 10 ml of conc. HCl, 100 ml of water and 7 g of dimethyl oxalate. Warm to between 60° and 70° with stirring, and when the soln. has become turbid heat on a sand bath. After not

less than 30 min. add 4 g of oxalic acid in 200 ml of water and set aside for 1 or 2 hr. (or overnight). Filter the cold soln., wash the ppt. 6 or 7 times with a 2% soln. of oxalic acid containing 40 ml of conc. HCl per litre, wash the ppt. from the filter with hot water and wash the filter first with hot HNO<sub>3</sub> and then with water. Evaporate the soln. to a small vol., add 15 or 20 ml of aqua regia, evaporate to 5 or 10 ml and repeat 2 or 3 times. Add 10 ml of HClO<sub>4</sub> and evaporate almost to dryness on a sand bath. Cool, add 100 ml of water and adjust the pH of the soln. to 2.4 to 2.6 with aq. NH<sub>3</sub> (to 2:4-dinitrophenol or with a pH meter). Add 5 drops of a 0.1% aq. soln. of arsenazo and titrate with 0.03 M EDTA (disodium salt) till the colour changes from lilac to pink. Standardise the EDTA soln. with Th(NO<sub>3</sub>)<sub>4</sub>. The accuracy when determining 5 to 7% of Th is 0.04% absolute.

C. D. KOPKIN

2681. Extraction and determination of thorium from sulphate and phosphate solutions with tri-n-octylphosphine oxide. W. J. Ross and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, 31 (11), 1847-1850.—The soln. is diluted with M HNO<sub>3</sub> until the SO<sub>4</sub><sup>2-</sup> concn. is reduced to 0.5 M or less, and the PO<sub>4</sub><sup>3-</sup> concn. is reduced to 0.06 M or less, and the soln. is made 2 M in NaNO<sub>3</sub>. Thorium is separated by extraction with tri-n-octylphosphine oxide soln. (0.1 M in cyclohexane, one-tenth of the volume of the aq. soln.). The extract is shaken with 0.3 M H<sub>2</sub>SO<sub>4</sub> and Th is determined photometrically at 545 m $\mu$  with thoron (1-o-arsenophenylazo-2-naphthol-3:6-disulphonic acid, sodium salt). The method is applicable to monazite sands. Interference by U can be avoided by oxidation to U<sup>VI</sup>, and Cr<sup>VI</sup> should be reduced to Cr<sup>III</sup>.

T. R. ANDREW

2682. Use of p-cresotic acid and its derivatives for the estimation of thorium and zirconium. S. P. Agarwal, R. C. Aggarwal and T. N. Srivastava (Chem. Dept., Univ. Lucknow, India). *Z. anal. Chem.*, 1959, 171 (2), 91-95 (in English).—Thorium and Zr are pptd. quant. with p-cresotic acid (2-hydroxy-5-methylbenzoic acid) and its nitro, sulpho, bromo, acetyl, benzoyl and hydrazine derivatives, as well as with 2-carboxymethoxy-5-methylbenzoic acid, provided the pH is between 4.00 and 5.23. The precipitant in all cases is 30 to 40 ml of a 2% aq. soln. of the Na salt, except for the sulpho and hydrazine derivatives, when a 5% aq. soln. is used. The ppt. are digested on the water bath for about 15 min., and are then filtered, washed with hot water and ignited to the oxide, which is weighed. Only certain ions, such as Fe<sup>3+</sup>, Cu<sup>2+</sup> and UO<sub>2</sub><sup>2+</sup> require a double pptn. These ions give coloured complexes.

H. M.

2683. Semi-quantitative spectrographic determination of some lanthanides in thoria. W. Trzebiatowski, A. Szaynok and P. Rozdział (Inst. of Phys. Chem., Dept. of Structural Res., Wrocław). *Chem. Anal.*, Warsaw, 1959, 4 (3), 563-569.—A method is described whereby trace amounts of La, Ce, Pr, Sm, Eu, Gd and Dy can be determined in thorium dioxide. The elements named are concentrated 1000-fold by extraction of thorium nitrate with tributyl phosphate in a continuous extraction apparatus (diagram given); concn. of lanthanides  $> 10^{-4}\%$  can be determined in a 100-g sample of thorium nitrate. W. B. MIAKOWSKI



**2684. Formaldehyde method for determining ammonia.** D. Stockdale (Univ. Chem. Lab., Cambridge, England). *Analyst*, 1959, **84**, 667-668.—The determination of an ammonium salt by addition of excess of formaldehyde to form hexamine and titration of the liberated acid is subject to two conditions tending towards inaccuracy, *viz.*, reversibility of the reaction, with consequent failure to reach completion unless the pH is increased, and a slowing of the reaction as the pH increases during titration. The procedure recommended is to dilute 40% formaldehyde soln. with an equal vol. of water, make slightly alkaline to phenolphthalein with NaOH soln., add an amount of the sample so that there is an excess of  $\approx 1$  ml of the diluted formaldehyde soln. per 10 ml of the final soln. and titrate immediately with NaOH soln. and add 2 ml in excess. Set aside the stoppered vessel for 15 min. and complete the titration with HCl soln. or, preferably, make the soln. slightly acid and back-titrate with NaOH soln. A. O. JONES

**2685. Effect of carrier humidity in the gas chromatography of ammonia.** L. A. du Plessis and A. H. Spong (Dept. of Chem., Univ. of Cape Town, S. Africa). *Chem. & Ind.*, 1959, (40), 1246.—In  $\text{NH}_3$  chromatograms recorded from long columns of Zn, Cu or Ni oleate supported on granular copper at  $\approx 170^\circ$ , two peaks are observed. The first, and lower, peak is ascribed to  $\text{H}_2\text{O}$  adsorbed from the carrier (N or  $\text{CO}_2$  at  $109^\circ$  to  $173^\circ$ ) and displaced by the  $\text{NH}_3$ . Rigorous drying of the carrier gas lowers the height of the moisture peak, but it does not vanish because of accidental re-contamination with  $\text{H}_2\text{O}$  in the apparatus. A packing of Accolube 93 C (zinc dialkyl phosphorodithioate in mineral oil) on glass beads at  $112^\circ$  also gives two peaks when the carrier is N saturated with  $\text{H}_2\text{O}$  at  $23^\circ$ .

W. J. BAKER

**2686. Argentimetric titrations, with redox indication. II. Determination of ammonia, ammonium ions and nitrogenous organic substances.** L. Erdey, K. Vigh and L. Pólos (Inst. for Gen. Chem., Tech. Univ., Budapest, Hungary). *Talanta*, 1959, **3** (1), 1-5 (in German).—Variamine blue B (C.I. Azoic Diazo Component 35) (I) is used as indicator in the titration, with standard  $\text{AgNO}_3$  soln., of the complex produced by  $\text{NH}_4^+$  with Na tetraphenylboron (II), which is quant. pptd. between pH 1 and 6.5 and then dissolved in acetone. Alternatively, back-titration of the excess of II may be used. The method is applicable to the determination of  $\text{NH}_4^+$  in Kjeldahl digests with an accuracy to within 1%. Interference by heavy-metal ions is minimised by pptn. at pH 2 or by the addition of EDTA (disodium salt). *Procedure*.—Dilute the aq. soln. (20 to 50 mg of  $\text{NH}_4^+$ ) so that 8 ml contains 1 mg of  $\text{NH}_4^+$ ; add 0.1 N acetic acid (1 ml per 50 ml of soln.) and 0.1 M aq. II (50% excess) in the cold, with stirring. Set aside for 5 min. and wash the ppt. with a satd. soln. of the II complex. Add acetone (6 to 60 ml), stir, add 2 N acetic acid (1 ml) and indicator (2 to 3 drops of a 1% soln. of I acetate) and titrate with 0.05 N  $\text{AgNO}_3$  to a violet endpoint.

**III. Determination of nitrate ions and nitro compounds.** L. Erdey, L. Pólos and Z. Gregorowicz. *Ibid.*, 1959, **3** (1), 6-13 (in English).—Nitrates are reduced with *ferrum reductum* (Ulsch, *Z. anal. Chem.*, 1891, **30**, 175) and  $\text{H}_2\text{SO}_4$  with  $\text{NiSO}_4$  as catalyst, and the  $\text{NH}_3$  so produced is treated with II; the resulting ppt. is dissolved in acetone, and titrated with 0.05 N  $\text{AgNO}_3$ , with I as indicator.

Alternatively, the  $\text{NO}_3^-$  may be reduced with Devarda's alloy in alkaline soln., and the  $\text{NH}_4^+$  recovered by distillation; EDTA (disodium salt) is added to the distillate to complex any traces of heavy metals that may have been carried over. Procedures are described for the determination of  $\text{NO}_3^-$  in the presence of organic matter, by treatment with salicylic acid,  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{S}_2\text{O}_8$ , and for the determination of N in organic azo, diazo and nitro compounds, by treatment with  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{H}_2\text{SO}_4$ , followed by Kjeldahl digestion. J. P. STERN

**2687. Determination of ammonium ions in ammonium bisulphite and neutral sulphite cooking liquors.** I. J. Polčín. *Zellstoff u. Papier*, 1959, **8** (4), 137-139.—The liquor, acidified to pH 3 with citric acid, is titrated potentiometrically with calcium hypochlorite soln., in the presence of KBr, until a potential increase is noted. The soln. is made alkaline (pH 8) with NaOH and  $\text{NaHCO}_3$  and titrated further until another distinct potential increase is reached. The first inflection point corresponds to the  $\text{SO}_3$  ( $\text{SO}_3^{2-}$ ) concn. and the second to the concn. of  $\text{NH}_4^+$ . This method is sufficiently precise and shorter than the conventional distillation method. (6 references.)

**II.** J. Polčín. *Ibid.*, 1959, **8** (5), 183-185.—A rapid gas-volumetric method for the determination of  $\text{NH}_4^+$  is described, based on the oxidation of  $\text{NH}_4^+$  to N by bromates and measurement of the N evolved. With proper precautions,  $\text{SO}_3$  and other reducing agents do not interfere. (4 references.) ABSTR. BULL. INST. PAPER CHEM.

**2688. Use of antazoline for identifying nitrate and nitrite.** E. G. C. Clarke (Dept. of Physiology, Royal Veterinary Coll., London). *Analyst*, 1959, **84**, 662-663.—Antazoline can be used to identify  $\text{NO}_3^-$  and  $\text{NO}_2^-$ , and either in the presence of the other. To test for  $\text{NO}_3^-$ , the  $\text{NO}_2^-$ , if present, are destroyed with sulphamic acid and a drop of a 5% soln. of antazoline hydrochloride in conc.  $\text{H}_2\text{SO}_4$  is added;  $\text{NO}_3^-$  produce a red colour. If 5 N HCl is used as solvent instead of conc.  $\text{H}_2\text{SO}_4$ , the yellow colour with  $\text{NO}_3^-$  develops, but not the red colour with  $\text{NO}_2^-$ . Oxidising agents,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{SCN}^-$  and arsenite interfere with the test for  $\text{NO}_3^-$ . In the test for  $\text{NO}_2^-$ ,  $\text{I}^-$  and  $\text{ClO}_3^-$  interfere only when present in large excess,  $\text{BrO}_3^-$  and some other oxidising agents form colours that mask the colour due to  $\text{NO}_2^-$ , and  $\text{SeO}_3$  inhibits the test. A. O. JONES

**2689. Nuclear magnetic resonance method for analysis of polyphosphoric acids.** J. C. Guffy and G. R. Miller (California Res. Corp., Richmond, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1895-1897.—The method described is as accurate as the best wet chemical methods and the sensitivity for showing very slight differences is even better. The method is rapid and about 15 min. per sample is required. K. A. PROCTOR

**2690. Polarographic determination of arsine in gas mixtures.** V. Vašák (Inst. Hyg. Ind. Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (10), 3500-3504 (in German).—The anodic polarographic wave of arsine was used for the determination. The supporting electrolyte was 900 ml of 95% ethanol mixed with 100 ml of N  $\text{NH}_4\text{NO}_3$ , which is a suitable solvent for arsine as well as a suitable polarographic medium. The method was used for the determination of arsine up to  $5 \times 10^{-4}$  M in gas mixtures. The results were in good agreement

with those obtained colorimetrically. Phosphine and stibine show similar polarographic behaviour and their waves coincide with that of arsine.

J. ZÝKA

**2691. Spectrophotometric determination of antimony with Rhodamine B.** R. E. Van Aman, F. D. Hollibaugh and J. H. Kanzelmeyer (Zinc Smelting Div., St. Joseph Lead Co., Monaca, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1783-1785.—Dissolve the sample (containing 5 to 20  $\mu$ g of Sb) in HCl-HNO<sub>3</sub> (10:1) (min. vol.), add conc. H<sub>2</sub>SO<sub>4</sub> (1 ml), evaporate to fumes, cool, take up in HCl (10 ml) and transfer to a 125-ml separating-funnel, washing the beaker with HCl (7 ml). Add 15 ml of diisopropyl ether and shake for 30 sec. Add 7 ml of H<sub>2</sub>O, mix, cool in a water bath (25°) for 10 min. and shake for 30 sec. Reject the aq. layer. Add Rhodamine B (C.I. Basic Violet 10) soln. (0.1 g in 41.7 ml of HCl diluted to 1 litre) (20 ml), shake for 30 sec. and measure the extinction of the ether layer, after centrifuging to remove droplets of H<sub>2</sub>O, at 550  $\mu$  against a H<sub>2</sub>O blank.

T. R. ANDREW

**2692. Volumetric determination of bismuth by means of potassium ferrocyanide in the presence of o-dianisidine.** H. Basińska and K. Orylska (Dept. of Inorg. Chem., Copernicus Univ., Toruń). *Chem. Anal., Warsaw*, 1959, **4** (3), 523-529.—The method is based on the direct titration of Bi in acetic acid soln., with standard K<sub>4</sub>Fe(CN)<sub>6</sub> soln., with o-dianisidine as a redox indicator. The soln. [containing Bi as Bi(NO<sub>3</sub>)<sub>3</sub>, 0.05 to 0.65 g] is neutralised with 0.5 M KOH until a permanent opalescence appears, which is then immediately cleared by the addition of 2 ml of glacial acetic acid, then 1 or 2 drops of a 1% soln. of K<sub>4</sub>Fe(CN)<sub>6</sub> and 3 to 10 drops of a 0.2% soln. of o-dianisidine are added, and the mixture is titrated with 0.1 M K<sub>4</sub>Fe(CN)<sub>6</sub>. The end-point (red to yellow-green) is sharp. The soln. can be neutralised with KOH, NaOH, Na<sub>2</sub>CO<sub>3</sub> or NaHCO<sub>3</sub>, but not with aq. NH<sub>3</sub> soln., which makes the end-point less sharp. The error does not exceed 0.2% as compared with that for the gravimetric bismuth oxydide method, and the time required is 15 min.

W. B. MIAKOWSKI

**2693. Potentiometric titration of bismuth with potassium ferrocyanide.** H. Basińska and Z. Orylski (Dept. Inorg. Chem., Toruń Univ., Poland). *Chem. Anal., Warsaw*, 1959, **4** (4), 685-670.—The sample soln. is acidified with acetic acid or HNO<sub>3</sub>, and measurements are taken in the cell mercury | Hg<sub>2</sub>Cl<sub>2</sub> + KCl | Bi soln. | platinum. The titration must be carried out in the absence of cations which form slightly soluble ppt. with [Fe(CN)<sub>6</sub>]<sup>4-</sup>. The error compared with gravimetric determination as bismuth oxydide is <1.0%.

L. SMAKOWSKI

**2694. New photometric determination of vanadium.** G. V. Rabovskii, T. F. Kuznetsova and V. A. Belonogova. *Zhur. Anal. Khim.*, 1959, **14** (5), 578-580.—Dissolve the sample (containing 0.1 to 1.0 mg of V) in 30 ml of aqua regia, and evaporate the soln. with 20 ml of H<sub>2</sub>SO<sub>4</sub> (1:1) to fumes of SO<sub>3</sub>. Add 20 to 30 ml of water and 1 or 2 drops of H<sub>2</sub>O<sub>2</sub> (to reduce Cr<sup>VI</sup>) and heat to boiling. Filter off the insoluble residue and wash it several times with hot water. Make the filtrate and wash liquors up to 100 ml, and to a 10-ml aliquot add 0.1 N KMnO<sub>4</sub> dropwise to a pink colour stable for 5 min. Remove the excess of permanganate with 0.05 M NaNO<sub>2</sub>, adding 1 drop in excess, and add 0.5 g of urea.

Transfer the soln. to a 50-ml flask, add 5 ml of H<sub>3</sub>PO<sub>4</sub> (4:1) and H<sub>2</sub>SO<sub>4</sub> (1:1) almost to the mark (these acids first being treated with KMnO<sub>4</sub>, NaNO<sub>2</sub> and urea), add 8 to 10 drops of a 0.1% soln. of N-phenylanthranilic acid, make up to volume with 50% H<sub>2</sub>SO<sub>4</sub> mix, and after 5 min. measure the extinction with a green filter. Barium diphenylaminesulphonate (1.5 to 2.0 ml) may be used instead of N-phenylanthranilic acid. Iron, U, Cr<sup>3+</sup> and Ni do not interfere. In determining V in samples of steel, the maximum relative error was 5.8%.

C. D. KOPKIN

**2695. Rapid spectrophotometric determination of vanadium in all materials.** P. Blanquet. *Chim. Anal.*, 1959, **41** (9), 359-367.—The catechol reaction of Patrovský (*Anal. Abstr.*, 1955, **2**, 1189) has been critically examined in order to eliminate many of the reported interferences. It is shown that in the final complex vanadium is present as VIII and not as VIV. *Procedure for concn. > 1%*—Dissolve the sample (0.25 g) in an appropriate acid mixture, or by fusion with Na<sub>2</sub>CO<sub>3</sub> and, after the addition of 5 to 10 ml of HClO<sub>4</sub>, evaporate to 1 to 2 ml; dilute with a little H<sub>2</sub>O and wash the soln. into a 100-ml flask. Add citric acid soln. (50%) (5 ml), ascorbic acid (0.5 g) and cyanide soln. [25 g of KCN and 12.5 g of EDTA (disodium salt) in 250 ml of aq. NH<sub>3</sub> (sp.gr. 0.92)] (20 ml, added rapidly under a hood). Boil gently for 1 to 2 min. under a hood, cool, dilute to vol. and mix. Allow the ppt. of KClO<sub>4</sub> to settle and decant the clear liquid (filter if necessary). Transfer 5 ml of the clear soln. to a 25-ml flask and dilute to vol. with reagent soln. [dissolve 35 g of catechol in 300 ml of H<sub>2</sub>O, add 50 ml of 50% citric acid soln., 2 g of ascorbic acid, 60 ml of aq. NH<sub>3</sub> (sp. gr. 0.92) and dilute to 500 ml; this soln. is rapidly oxidised and should be prepared within 2 hr. of use, unless protected from air by a layer of xylene, when it may be stored for several days]. Mix and set aside for 20 min. Determine the extinction at 800  $\mu$  against a blank. A precision of  $\pm 0.01\%$  for 1% of V is claimed. Interferences have been studied in detail for most elements of the Periodic Table. Most do not interfere; the remainder of those tested do not interfere in concn. up to 10%.

T. R. ANDREW

**2696. Separation of niobium and tantalum with phenylarsonic acid.** A. K. Majumdar and A. K. Mukherjee (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, **21** (4), 330-333.—Soln. (150 ml) of Ta<sub>2</sub>O<sub>5</sub> (8 to 190 mg) and Nb<sub>2</sub>O<sub>5</sub> (5 to 180 mg) are treated with ammonium oxalate (25 times the wt. of Ta<sub>2</sub>O<sub>5</sub> present) and the acidity is adjusted to 5% (v/v) of H<sub>2</sub>SO<sub>4</sub>. The soln. is boiled, treated with an excess of phenylarsonic acid (I) (5% soln.) and boiling is continued for 2 to 5 min. The ppt. of Ta phenylarsonate is filtered off, washed with a soln. of 0.5 g of I and 1 g of NH<sub>4</sub>NO<sub>3</sub> in 100 ml of water, dried, ignited, and weighed as Ta<sub>2</sub>O<sub>5</sub>. The filtrate is heated to boiling, ammonium acetate is added to raise the pH to 5.0 and the Nb is pptd. When the ratio of Nb<sub>2</sub>O<sub>5</sub> to Ta<sub>2</sub>O<sub>5</sub> is <1:1 the amount of ammonium oxalate initially added prevents quant. pptn. of Nb, which must then be determined by pptn. with cupferron. When this ratio is >2:1, re-precipitation of Ta is necessary for complete separation. If EDTA is also added the procedure serves for the separation of Ta from a number of ions, but those of Ti, Zr, Pb, Ba and Sr interfere, and Sn<sup>2+</sup>, Th<sup>4+</sup> and UO<sub>2</sub><sup>2+</sup> make a second pptn. necessary.

H. N. S.



**2697. Extraction and separation of niobium and titanium from oxalate solutions by ion exchange.**

I. D. Fridman and I. N. Yudina. *Zhur. Prikl. Khim.*, 1959, **32** (9), 1914-1919.—A study of the adsorption of Nb and Ti from an 8 to 10% oxalate soln. by the cation-exchange resin KU-2 (H<sup>+</sup> form) and the anion-exchange resin EDE10P (Cl<sup>-</sup> form) has shown that in this soln. both Nb and Ti are in the form of complex anions with similar adsorption properties. There is no cationic adsorption of Nb and that of Ti is very weak. *Procedure*—Anionite EDE10P (Cl<sup>-</sup> form, 0.4 to 0.1 mm mesh) (10 g) (prepared by immersing it in water for 2 to 3 hr., then in 5% NaOH soln. for 2 to 3 hr., washing with water and finally immersing in 5% HCl for 2 to 3 hr.) was mixed with the test soln. (containing 7.2 g of Nb<sub>2</sub>O<sub>5</sub>, 5.6 g of TiO<sub>2</sub>, 7.1 g of Fe<sub>2</sub>O<sub>3</sub> and 90 g of oxalic acid per litre) (100 ml) and stirred mechanically for 1 hr. at 140 r.p.m. The resin with the adsorbed Nb and Ti was then transferred to a separating-funnel of 28 mm diam. Gravity elution at 2 ml per min was used. The best eluent for Nb was 2 M NaCl, which should be freed from K<sup>+</sup> and other ions by passage through KU-2 cationite (Na<sup>+</sup> form). The Nb content of the eluate was  $\approx$  93 to 97%, and that of Ti  $\approx$  9 to 18%, of the initial concn. The residual Ti was recovered by eluting with M HCl. To decrease the Ti content of the eluate containing Nb, it was passed through fresh resin. The eluate thus obtained contained only traces of TiO<sub>2</sub>. By the technique described, Nb<sub>2</sub>O<sub>5</sub> of 98% purity, containing 1.8 to 2% of TiO<sub>2</sub>, was obtained from a soln. containing Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> in the ratio of 1:0.8. W. ROUBO

**2698. Spectrophotometric determination of niobium in tantalum.** K. S. Bergstresser (Univ. of Calif., Los Alamos Sci. Lab., N.M., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1812-1814.—The ion-exchange separation of Cabell and Milner (*Anal. Abstr.*, 1956, **3**, 386) is followed by co-pptn. of the eluted Nb on Al(OH)<sub>3</sub>, and subsequent determination of Nb by ether extraction of the thiocyanate complex. From 4 to 9  $\mu$ g of Nb has been determined in tantalum (up to 100 mg) with an average error of 0.05  $\mu$ g of Nb. T. R. ANDREW

**2699. Extraction of tantalum and niobium by cyclohexanone from sulphate solutions.** Ya. G. Gorchchenko, M. I. Andreeva and A. G. Babkin. *Zhur. Prikl. Khim.*, 1959, **32** (9), 1904-1913.—A study of the extraction of Ta and Nb from a H<sub>2</sub>SO<sub>4</sub>-(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-NH<sub>4</sub>F soln. is presented. The concn. of Ta in the aq. phase can be reduced to 0.03 to 0.04% of its initial concn., while the extraction of Nb is  $\approx$  60 to 70%. Niobium can be re-extracted from the cyclohexanone phase by a mixture of H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> without extracting the Ta. W. ROUBO

**2700. Chemical analysis of tantalum-niobium ores and concentrates.** S. Král (SONP, Kladno, Czechoslovakia). *Hutn. Listy*, 1959, **14** (9), 807-809.—Detailed procedures are given for the determination of all components of these materials of importance in metallurgical analysis; SiO<sub>2</sub> is determined by treatment of the sample with H<sub>2</sub>SO<sub>4</sub> and HF; the remaining oxides of Nb, Ta, Ti and Zr are fused with KHSO<sub>4</sub> and then separated as cupferronates; Ta is determined as Ta<sub>2</sub>O<sub>5</sub>, Nb volumetrically with KMnO<sub>4</sub> after passage through a Jones reductor, Ti colorimetrically with H<sub>2</sub>O<sub>2</sub>, and Zr gravimetrically as pyrophosphate. The same soln. can be used for the colorimetric

determination of Fe with thiocyanate. A second aliquot is used for the determination of Al (gravimetrically as Al<sub>2</sub>O<sub>3</sub>) and As (by titration with KBrO<sub>3</sub> after distillation); Sn is determined polarographically in a medium of HCl and hydrazine, after reduction to Sn<sup>2+</sup>. The polarographic method is also used for the determination of Ni and Cu. For the determination of Mn, the method of Proctor and Smith is recommended. Procedures are also given for the determination of P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub> and CO<sub>2</sub>. J. ZVKA

**2701. Determination of free sulphur by reduction to hydrogen sulphide.** I. I. Volkov (Inst. of Oceanology, Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 592-594.—To determine free sulphur in rocks, extract a sample with acetone for at least 16 hr. and make up to 50 ml with acetone. Evaporate an aliquot to dryness on a water bath, without allowing the acetone to boil. Oxidise the S to sulphate by treating with 2 or 3 ml of a soln. of Br in CCl<sub>4</sub> (2:3) for 10 to 15 min. at room temp., with occasional stirring. Add 5 ml of conc. HNO<sub>3</sub>, stir for 10 to 15 min., and heat on a water bath to remove most of the Br, and then evaporate to dryness. Add 3 ml of HCl and again evaporate to dryness to remove HNO<sub>3</sub>. Add not more than 0.1 g of KCl and 3 ml of HCl and evaporate once more. Add a few drops of HCl, transfer the residue to the reducing-apparatus container with hot water and evaporate to dryness. To the residue add 8 ml of reducing mixture (Sn<sup>2+</sup> and H<sub>2</sub>PO<sub>4</sub>; cf. Volkov and Ostroumov, *Anal. Abstr.*, 1959, **6**, 2565) in the reducing-apparatus filled with CO<sub>2</sub>, pass CO<sub>2</sub> for 4 or 5 min., gradually heat to 300° and maintain at this temp. for 25 to 30 min. Absorb the liberated H<sub>2</sub>S in a soln. of Cd acetate, pour the resulting suspension into acidified 0.01 N iodine and titrate the excess of iodine with 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. Sulphide and sulphate sulphur are removed by treating the sample with dil. HCl in a current of CO<sub>2</sub>. The method has been tested on a standard soln. of S in acetone, and on various rock samples. In determining 0.10 to 5.12 mg of S in the standard soln. the max. error was  $\pm$  0.04 mg. In determining 0.05 to 3.08% of S in rock samples, almost quant. results were obtained. C. D. KOPKIN

**2702. Gas-chromatographic analysis of hydrogen sulphide, sulphur dioxide, mercaptans [thiols] and alkyl sulphides and disulphides.** D. F. Adams and R. K. Koppe (Air Pollution Res. Sect., Div. of Ind. Res., State College of Washington, Pullman, U.S.A.). *TAPPI*, 1959, **42**, 601-605.—Complex mixtures of volatile sulphur-containing compounds can be separated and identified, with columns 6 ft.  $\times$  0.25 in. prepared from packings of 60 g of stationary-phase solvent and 70 g of 30 to 60 mesh Chromosorb. Runs were started at an initial column temp. of 30° which was rapidly increased to 100° after elution of diethyl sulphide. A series of chromatograms with an 8-component mixture on four typical Triton columns confirmed the assumption that the longer the solvent side chain, the longer the retention time for SO<sub>2</sub> and the shorter the retention time for thiols and sulphides. Triton X-45 behaved anomalously and is not recommended as a solvent for mixtures containing SO<sub>2</sub> and methanethiol. Triton X-305 (OPE 30), having a polyoxyethylene side-chain of approx. 30 units, produces the best separation with min. emergence time and max. water retention time to prevent masking of significant areas of

the elution curve. If the sample contains large amounts of water it may be necessary to separate this before the analysis.

R. AICHER

**2703. Simplified rapid method for determination of sulphate by means of ion exchange.** J. A. Mikes and J. Szantó (Res. Inst. for the Plastics Industry, Budapest, Hungary). *Talanta*, 1959, **3** (1), 105-107 (in German).—For the rapid determination of  $\text{SO}_4^{2-}$  in  $\text{CuSO}_4$ , the  $\text{SO}_4^{2-}$  are exchanged for  $\text{Cl}^-$  on Mykion PA anion-exchange resin and are then titrated with  $\text{AgNO}_3$  by Mohr's method, or, if the soln. is acid, by Volhard's method. Interfering cations are exchanged for  $\text{Na}^+$  on Mykion PS cation-exchange resin,  $\text{PO}_4^{3-}$  are removed by  $\text{MgO}$ , and any  $\text{Cl}^-$  in the original soln. are determined separately. An apparatus with two columns in series is illustrated, in which the determination can be completed in 20 min., the accuracy on 8 mg of  $\text{CuSO}_4$  being to within  $\pm 1\%$ .

J. P. STERN

**2704. Rapid method for the indirect determination of the sulphate ion in sulphuric acid and pyrites by flame photometry.** V. Nicolaescu and S. Ioan. *Rev. Chim., Bucharest*, 1959, **10** (10), 610.—The  $\text{SO}_4^{2-}$  are pptd. by an excess of  $\text{BaCl}_2$  soln., and the residual  $\text{Ba}^{2+}$  is determined. *Procedure for  $\text{H}_2\text{SO}_4$* —The  $\text{H}_2\text{SO}_4$  soln. (10 ml) is heated to boiling and treated with a measured excess of 0.1 N  $\text{BaCl}_2$ . After 2 hr. on a hot-water bath the mixture is transferred to a 250-ml flask and an aliquot is filtered through a dry filter. The excess of Ba is determined by a Zeiss Jena flame photometer model III. *Procedure for pyrites*—The sample (0.5 to 3 g) is dissolved in the usual manner. The soln. is oxidised with 40 ml of a mixture of  $\text{HNO}_3$  and  $\text{HCl}$  (3:1). The soln. is evaporated to dryness; the residue is moistened with 5 ml of conc.  $\text{HCl}$  and evaporated, and the operation is repeated twice to render the  $\text{SiO}_2$  insoluble. The residue is then treated with a minimum of 2 N  $\text{HCl}$  and  $\approx 50$  ml of  $\text{H}_2\text{O}$ , boiled, and treated with  $\text{ZnO}$  in slight excess to remove interfering heavy metals. The ppt. is filtered off and washed, with suction, on a G4 crucible, and the filtrate and washings are diluted to 500 ml. An aliquot (50 ml) is then treated as described above. The relative errors over a range of 2.8 to 41.0% of  $\text{SO}_4^{2-}$  vary from  $-1.2\%$  to  $-5.7\%$ .

H. SHER

**2705. Iodimetric method for determination of persulphates.** N. Wahba, M. F. El Asmar and M. M. El-Sadr (Biochem. Dept., Fac. of Med., Abbassia, Ain-Shams Univ., Cairo). *Anal. Chem.*, 1959, **31** (11), 1870-1871.—Potassium persulphate (0.2 to 0.3 g), in 33% (v/v) acetic acid, liberates iodine from KI soln. (16%) (10 ml) in 1 hr., when the mixture is kept in the dark under  $\text{CO}_2$ . The presence of  $\text{FeCl}_3$  (0.003 to 0.006% in the acetic acid) reduces the time of reaction to 15 min. The liberated iodine may be titrated with  $\text{Na}_2\text{S}_2\text{O}_3$  soln.

T. R. ANDREW

**2706. Separation of selenium and tellurium.** V. I. Plotnikov (All-Union Sci.-Res. Mining and Metall. Inst. of Non-ferrous Metals, Ust'-Kamenogorsk). *Zhur. Anal. Khim.*, 1959, **14** (5), 595-597.—By using the radioactive isotope  $^{127}\text{Te}$  and an unspecified radioactive isotope of Se, it is shown that Te, both as tellurous and telluric acids, is quant. co-pptd. with  $\text{Fe}(\text{OH})_3$ , while only about 1% of Se as selenic acid is co-pptd. with  $\text{Fe}(\text{OH})_3$  in an ammoniacal soln. (pH 9.4 to 9.7). This procedure may be used to separate  $\text{Te}^{\text{VI}}$  and  $\text{Se}^{\text{VI}}$ .

C. D. KOPKIN

**2707. Amperometric micro-determination of selenium.** R. Jensen (Lab. de Chim. Biol. et Méd., Faculté de Méd. et de Pharm. Bordeaux). *Chim. Anal.*, 1959, **41** (10), 394-396.—The Se is collected by distillation as  $\text{SeOCl}_2$  in a  $\text{HCl}-\text{H}_2\text{SO}_4$  medium in the presence of free Br (Dolique and Herahia, *Bull. Soc. Chim. France*, 1946, **13**, 44). When the soln. has been diluted so that the  $\text{HCl}$  is 2 N, the excess of Br is titrated amperometrically with 0.1 N and 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$ . A known excess of 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$  is then added to react with the Se, according to the reaction described by Norris and Fay (*Amer. Chem. J.*, 1896, **18**, 705). The excess of  $\text{Na}_2\text{S}_2\text{O}_3$  is titrated amperometrically with 0.01 N iodine. The results show a spread of  $\approx 10\%$ . The need for a rotating electrode is obviated by using a simple cell (illustrated) and stirring the soln. magnetically; 1 equiv. of  $\text{Na}_2\text{S}_2\text{O}_3 = 19.7 \mu\text{g}$  of Se.

J. H. WATON

**2708. Determination of certain trace impurities in high-purity selenium.** O. E. Zvyagintsev and V. I. Shamaev (D. I. Mendeleev Moscow Chem. and Technol. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (5), 603-605.—The sample ( $\approx 1$  g) and standards are irradiated in a nuclear reactor to produce radioactive isotopes by the ( $n, \gamma$ ) reaction. The sample and standards are dissolved in  $\text{HNO}_3$ , carriers for As, Cu, Ga, Sb, Te and Cd are added (10 to 20 mg of each element), and these elements are separated chemically. Detailed directions are given for each separation. The final products are weighed and their activity measured. Radiochemically pure separations are achieved, in chemical yields of 50 to 70% for Cu, As and Cd, 30 to 50% for Te, and 25 to 35% for Sb and Ga. The accuracy of the determination of the individual elements is 10 to 25%. One sample was analysed and found to contain Te  $1.2 \times 10^{-4}\%$ , Ga  $< 10^{-7}\%$ , Cd  $4.5 \times 10^{-6}\%$ , As  $1.9 \times 10^{-5}\%$ , Cu  $6 \times 10^{-6}\%$ , and Sb  $1.6 \times 10^{-6}\%$ .

C. D. KOPKIN

**2709. Contributions to the chemistry of selenium and selenium compounds. II. Iodimetric determination of selenocyanate.** E. Schulek and L. Barcza (Inst. of Anal. Chem., Eötvös Univ., Budapest, Hungary). *Talanta*, 1959, **3** (1), 23-26.—When  $\text{SeCN}^-$  are oxidised by Br to  $\text{SeO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  do not interfere, but  $\text{Br}^-$  affect the equilibria set up and prevent the completion of the oxidation. This interference is eliminated either (i) by the addition of  $\text{Na}_2\text{WO}_4$  (to give a stable heteropoly acid) while maintaining low concn. of  $\text{H}^+$  and  $\text{I}^-$ , or (ii) by distillation and determination of the  $\text{BrCN}$  formed. The accuracy on 2 mg of Se in the presence of  $> 600$  mg of KBr is then within  $\pm 0.4\%$ . *Procedure (i)*—Dilute the  $\text{SeCN}^-$  soln. (0.4 to 4 mg of Se) to 40 to 45 ml, add  $\text{Na}_2\text{WO}_4$  (0.2 g) and neutralise to methyl red. Add satd. bromine water to a brownish-yellow colour, set aside for 2 to 3 min., add 5% phenol soln. (2 to 4 ml), set aside for 4 to 5 min. and acidify with 10%  $\text{HClO}_4$  soln. (2 ml). Add KI (0.1 to 0.2 g), set aside for 20 min., and titrate the liberated iodine with 0.01 N  $\text{Na}_2\text{S}_2\text{O}_3$ . (ii)—Neutralise the diluted  $\text{SeCN}^-$  soln., add an excess of bromine water, and distil for 4 to 5 min. in an all-glass apparatus, with the delivery tube dipping under water. To the distillate add the phenol soln., set aside, add the  $\text{HClO}_4$  and KI, and titrate after 20 min.

**III. Micro-determination of selenite through cyanogen bromide.** E. Schulek and L. Barcza. *Ibid.*, 1959, **3** (1), 27-30.—The reduction of  $\text{Se}^{\text{VI}}$  at pH 5 to colloidal Se with ascorbic acid, followed

by the addition of KCN yields  $\text{SeCN}^-$  which can be determined as described above after adding  $\text{H}_2\text{BO}_3$  and boiling off excess of HCN. The accuracy for 0.8 to 8.0 mg of  $\text{Na}_2\text{SeO}_3$  is within  $\pm 0.5\%$ .

**IV. Detection and determination of minute amounts of selenite in presence of selenate.** E. Schulek and L. Barcza. *Ibid.*, 1959, **3** (1), 31-33.—Ascorbic acid reduces  $\text{SeO}_3^{2-}$  to colloidal Se within 10 min. at pH 6, room temp. and low halide ion concn. without affecting  $\text{SeO}_4^{2-}$ ; 10  $\mu\text{g}$  of  $\text{SeO}_3^{2-}$  can thus be detected in 10 ml of soln. in the presence of  $> 100$  mg of  $\text{SeO}_4^{2-}$ . The colloidal Se from 0.8 to 8 mg of  $\text{SeO}_3^{2-}$  is determined as described above, with an accuracy within  $\pm 1\%$  in the presence of  $> 100$  mg of  $\text{SeO}_4^{2-}$ .

J. P. STERN

**2710. Determination of carbon in chromium carbide ( $\text{Cr}_3\text{C}_2$ ).** V. Dufek and Z. Marek (VÚPM, Vestec u Prahy, Czechoslovakia). *Hutn. Listy*, 1959, **14** (10), 909-912.—The method is based on the fact that at  $600^\circ$  to  $620^\circ$  only the free carbon is oxidised whereas the carbide remains unattacked. A modified method in which only one portion of the sample is used is recommended: 0.3 to 0.5 g of chromium carbide is heated for 60 min. at  $560^\circ$  (free C) and then for 90 min. at  $1300^\circ$  to  $1450^\circ$  (combined C). The  $\text{CO}_2$  formed is determined gravimetrically by absorption in the usual manner.

J. ZÝKA

**2711. Reaction of hexavalent uranium with EDTA (disodium salt).** D. I. Ryabchikov, P. N. Palei and Z. K. Mikhailova (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 581-587.—The reaction of  $\text{UO}_2^{2+}$  with EDTA (disodium salt) (I) is studied by ion exchange, spectrophotometrically and conductometrically. The ion-exchange experiments on the cationite KU-2 and the anionite EAE-10 showed that at pH 1.7 the U is present as a cation, at pH 5.5 an anionic complex is present, and at pH 8.0 the U is practically completely complexed as a complex anion. Soln. of  $\text{UO}_2^{2+}$  containing I absorb at 400 to 500  $\mu\mu$ , with a maximum at about 416  $\mu\mu$ . Increase of pH and of the concn. of I increase the extinction of the soln., the maximum at pH 3.8 to 6.0 being at about 436 to 437  $\mu\mu$ ; the maximum is greatest at pH 5.5 to 5.9, but at this pH the complex anion is not sufficiently stable for all the U to be complexed. Conductimetric titration of 0.00084 M  $\text{UO}_2(\text{NO}_3)_2$  with 0.05 and 0.1 M I showed breaks in the titration curves at the molar ratio of I to  $\text{UO}_2^{2+}$  of 0.5, indicating the formation of a compound of this composition. It is suggested by the results that two compounds are formed in soln. containing I and  $\text{UO}_2^{2+}$ , containing these components in the molar ratios 1:1 and 1:2, respectively. By adding a deficiency and an excess of EDTA (ammonium salt) (183.5 mg and 734 mg of EDTA) to a soln. of  $\text{UO}_2\text{Cl}_2$  (299 mg of U), and adjusting the pH to 4 and 5.5, respectively, adding a mixture of methanol and acetone (2:1), filtering off the yellow ppt. and washing them with methanol, with acetone and with ether and drying in air, two compounds were prepared, of composition approximating to  $(\text{UO}_2)_2\text{R}\cdot 3\text{H}_2\text{O}$  and  $(\text{NH}_4)_2(\text{UO}_2)_2\text{R}\cdot 3\text{H}_2\text{O}$ , where R is the doubly charged ion derived from I.

C. D. KOPKIN

**2712. Solvent extraction of uranium, with chloroform, as acetylacetonate.** Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Kyoto). *Bull. Inst.*

*Chem. Res., Kyoto Univ.*, 1959, **37** (4), 226-231.—The separation of U from other metals with EDTA as masking agent is described. *Procedure*—To the sample soln. add 1 ml of 10% EDTA (disodium salt) soln. and 5 to 10 g of NaCl. Dilute to about 30 ml, adjust the pH to 7, add 20 ml of 5% aq. acetylacetonate soln. and adjust to pH 7. Dilute the soln. to 50 ml and extract the U acetylacetonate with 10, 5 and 5 ml of acetylacetonate-chloroform soln. (1:99). The recovery is 90 to 95% of the U in the organic layer, and only 0.2% of Th is extracted. For the determination of uranium, the organic phase is air-dried, treated with  $\text{HClO}_4$  and evaporated nearly to dryness. The residue is dissolved in 5 N  $\text{H}_2\text{SO}_4$  (0.5 ml) and a few ml of  $\text{H}_2\text{O}$ . Stannous chloride soln. (freshly prepared) (2 ml) and 50% KSCN soln. (5 ml) are added and the soln. is made up to 20 ml with  $\text{H}_2\text{O}$ . The extinction is measured at 365  $\mu\mu$  against a reagent blank. The colour is stable for at least 1 hr.

D. C. ARMSWORTH

**2713. Spectrophotometric determination of uranium, by solvent extraction, as acetylacetonate.** Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Kyoto). *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37** (4), 237-244.—*Procedure*—To the sample soln., containing 200  $\mu\text{g}$  to 1500  $\mu\text{g}$  of U, add 2 ml of 10% EDTA (disodium salt) soln. and an equiv. amount of  $\text{CaCl}_2$  soln. Adjust the pH to  $\approx 7$ , add 5% aq. acetylacetonate soln. (2 ml), adjust to pH 6.5 to 7 and dilute to  $\approx 50$  ml with  $\text{H}_2\text{O}$ . Extract with 20 ml of butyl acetate and dehydrate the organic phase with  $\text{Na}_2\text{SO}_4$ ; measure the extinction at 360 or 365  $\mu\mu$  against a reagent blank. The colour is stable for at least 24 hr. and Beer's law is obeyed up to 70 p.p.m. of U. Titanium, Cr, Mn, Fe and large amounts of Cu interfere, but Mo, V and W do not.

D. C. ARMSWORTH

**2714. Determination of microgram quantities of uranium in thorium.** V. T. Athavale, L. M. Mahajan, N. R. Thakoor and M. S. Varde (Atomic Energy Estab., Trombay, Bombay, India). *Anal. Chim. Acta*, 1959, **21** (4), 353-356.—Uranium is separated from  $\text{ThO}_2$  as a preliminary to its fluorimetric determination. In a soln. of the sample the Th is complexed with EDTA and the  $\text{UO}_2^{2+}$  are extracted with a 5% (v/v) soln. of tributyl phosphate (I) in kerosine or white spirit. The I is first extracted with 5% aq.  $\text{Na}_2\text{CO}_3$  soln. and its soln. is equilibrated by shaking with dil.  $\text{HNO}_3$  (pH 2.5). *Procedure*—Dissolve a sample that contains the equiv. of 1 g of  $\text{ThO}_2$  in conc.  $\text{HNO}_3$  with a few drops of dil. HF (2%), evaporate to dryness, add a few ml of conc.  $\text{HNO}_3$  and again evaporate to dryness. Dissolve the residue in 5 ml of water, add 1.6 g of EDTA (disodium salt) and adjust to pH 2.5. Add 16 g of  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ , dilute to 25 ml and extract the soln. with five 20-ml portions of the soln. of I. Wash the combined extracts with 3 portions of saturated  $\text{NH}_4\text{NO}_3$  soln. of pH 2.5. Re-extract the U from the organic solvent with one 10-ml portion of water, one 10-ml portion of 5% ammonium carbonate soln. and finally with two 10-ml portions of 0.5% ammonium carbonate soln. Acidify the combined extracts with  $\text{HNO}_3$ , evaporate to dryness, ignite at  $600^\circ$  and determine the U fluorimetrically (cf. Price *et al.*, *Brit. Abstr. C*, 1953, 303) in the residue. Known quantities of U from 1 to 10  $\mu\text{g}$  are determined with max. errors of  $-0.12$  to  $+0.09 \mu\text{g}$ . The sample size can be increased to 2.5 g to permit the determination of 0.4 p.p.m. of U. None of the following ions interferes— $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ce}^{4+}$ ,



Ti<sup>4+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Sn<sup>2+</sup>, Bi<sup>3+</sup>, Cr<sup>3+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, F<sup>-</sup>, MoO<sub>4</sub><sup>2-</sup>, VO<sub>3</sub><sup>-</sup>.  
H. N. S.

**2715. Use of thorium nitrate in the titration of fluorine after its separation from uranium by ion-exchange resins.** F. Vogliotti (Lab. Ric., Porto Marghera, Italy). *Energia Nucleare*, 1959, **6**, 661-664.—The specific determination of F in NaUF<sub>6</sub> and UF<sub>6</sub> with cationic resins involves the following procedure. The sample under test is decomposed with NaOH and H<sub>2</sub>O<sub>2</sub>. The soln. is passed through a column filled with a cation-exchange resin IR 120 and the anionic soln. obtained is titrated with standard 0.05 N Th(NO<sub>3</sub>)<sub>4</sub>. The procedure for the prep. of standard Th(NO<sub>3</sub>)<sub>4</sub> soln. and the method of conversion of the resin into a hydrogen form is also given. A general description of the method of analysis, discussion of the results obtained, and the main advantages of the new method are presented. *NUCL. SCI. ABSTR.*

**2716. Detection of fluorides on paper chromatograms by colour reactions.** A. Lewandowski and W. Szczepaniak (Dept. of Gen. Chem., A. Mickiewicz Univ., Poznań). *Chem. Anal., Warsaw*, 1959, **4** (3), 535-537.—The method, based on the reaction of fluorides with aluminium hydroxide, according to the equation  $6\text{NaF} + \text{Al}(\text{OH})_3 \rightarrow \text{Na}_3\text{AlF}_6 + 3\text{NaOH}$ , permits the detection of F<sup>-</sup> (< 1 µg on a spot of 6 mm diam.) when a suitable pH indicator (e.g., phenol red) is used. *Procedure*—The chromatogram is treated with a suspension of Al(OH)<sub>3</sub> and indicator, and within seconds the spots become visible on a pale background. Phosphates lower the sensitivity but can be separated by chromatography on Whatman No. 1 paper with butanol-acetone-H<sub>2</sub>O (1:6:3). Hydroxides of other metals (e.g., Be and Zr) can also be employed. A stable suspension of Al(OH)<sub>3</sub> is prepared by mixing a soln. of an aluminium salt with an anion-exchange resin (OH form). After 2 hr. the suspension is decanted off and the indicator is added just before use.

W. B. MIASKOWSKI

**2717. Determination of fluorine as lithium fluoride.** E. R. Caley and G. R. Kahle (McPherson Chem. Lab., Ohio State Univ., Columbus). *Anal. Chem.*, 1959, **31** (11), 1880-1881.—Fluoride (20 to 200 mg) in 15 to 40 ml of aq. soln. may be determined by heating the neutralised soln. to 70°, adding an equal vol. of LiCl soln. (3% in 95% ethanol), allowing to cool to room temperature, filtering in a sintered glass filter, washing the ppt. until free from Cl<sup>-</sup> with 50% ethanol saturated with LiF, then with 5 ml of ethanol (95%), drying at 110° and weighing as LiF. Sulphate does not interfere.

T. R. ANDREW

**2718. Determination of free hydrofluoric acid in tantalum-niobium-hydrofluoric acid solutions by near-infra-red spectrophotometry.** W. J. Allan and A. R. Gahler (Technol. Dept., Union Carbide Metals Co., Niagara Falls, N.Y.). *Anal. Chem.*, 1959, **31** (11), 1778-1783.—Measurement of absorption at 1835 mµ in a poly(tetrafluoroethylene) cell with sapphire windows can be used to determine HF in soln. The absorption spectrum shows a shift towards higher wavelengths as the cell size decreases and a path length of 0.04 cm was chosen. Beer's law is followed up to 10 N HF. Hydrochloric acid, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HClO<sub>4</sub> all show absorption at 1835 mµ, suggesting that the method could be applied to the determination of total free inorganic acid. Experiments with NbF<sub>5</sub> and TaF<sub>5</sub>

in HF indicate the formation of other ionic species at various HF concn. Interferences have been studied, and some observations are added on the absorption spectra of niobium fluorides in HF in the near-ultra-violet region (350 to 400 mµ).

T. R. ANDREW

**2719. Precipitation of manganese in silicate-rock analysis.** P. G. Jeffery and A. D. Wilson (D.S.I.R., Lab. of the Gov. Chemist, Geol. Survey and Museum, S. Kensington, London). *Analyst*, 1959, **84**, 663-665.—Unless special precautions are taken, manganese, during a silicate analysis, is distributed among the ppt. obtained with aq. NH<sub>4</sub> oxalate and PO<sub>4</sub><sup>3-</sup>. To avoid this, the Mn is pptd. with the members of the Fe group in the presence of an oxidising agent. A comparative study is made of two recommended oxidising agents, viz. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and Br. The (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>-aq. NH<sub>4</sub> mixture effected the better separation and provided the additional advantages that sulphide pptn. is avoided and that the Mg ppt. is free from Mn. There is no retention of Ca or Sr in the Fe group, but partial pptn. of Ba does occur. Pptn. of Mn by the aq. NH<sub>4</sub>-Br procedure was significantly less complete.

A. O. JONES

**2720. Determination of manganese in beryllium compounds (fluoride, hydroxide and ammonium fluoroberyllate).** A.E.R.E. Report AERE-AM 52, 1959, 3 pp.—The method is based on standard analytical practice and has been written with full details by J. Walkden.

**2721. Studies in polarography. IV. Reduction of manganate at the dropping-mercury electrode.** I. M. Issa, R. M. Issa and I. F. Hewaidy (Chem. Dept., Assiut Univ., Egypt). *Rec. Trav. Chim. Pays-Bas*, 1959, **78** (11), 889-898.—Reduction of MnO<sub>4</sub><sup>2-</sup> to Mn<sup>2+</sup> and then to Mn occurs at the dropping-mercury electrode in 0.05 to slightly less than 1.0 N NaOH, the diffusion current of the two main waves decreasing uniformly with concn. of NaOH, viz. between 0.05 and 0.5 N at -1.5 V (the first wave) and between 0.05 and 1.0 N at -1.85 V (the second wave). In N NaOH the reduction proceeds via Mn<sup>3+</sup> and Mn. The second wave is better developed at lower than at higher alkalinities. From  $2.5 \times 10^{-4}$  to  $2 \times 10^{-3}$  M MnO<sub>4</sub><sup>2-</sup> can be determined from the polarograms in 0.1 and 0.5 M NaOH, provided that an excess of formic acid (used for reduction of MnO<sub>4</sub><sup>2-</sup> to MnO<sub>4</sub><sup>3-</sup>) is not present. The results generally confirm those of den Boef and Poeder (*Ibid.*, 1958, **77**, 1071).

W. J. BAKER

**2722. Solvent extraction in ferrous analysis.** W. E. Clarke (B.C.I.R.A., Bordesley Hall, Alvechurch, Birmingham, England). *J. Res. Brit. Cast Iron Ass.*, 1959, **7** (14), 813-823.—The principles of solvent-extraction separations are discussed and procedures developed by the B.C.I.R.A. for the analysis of cast iron and foundry materials are described under two main headings—(i) those in which interfering elements are removed by extraction with isobutyl acetate, acetylacetone, and Na diethyldithiocarbamate; and (ii) those in which the elements to be determined are extracted, e.g., Mo as thiocyanate, Ce and Al as the 8-hydroxyquinoline complexes, Co as the 2-nitroso-1-naphthol complex, Al as the cupferrate, Pb and Bi as the diethyldithiocarbamates, and Fe as the acetylacetonate. The spectrophotometric determination of Cu as diethyldithiocarbamate and Pb as dithizonate are among other methods mentioned.

C. H. COWPER-COLES

**2723. Solvent extraction of iron as acetylacetonate with chloroform.** Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Kyoto). *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37** (4), 232-236.—The separation of Fe from Ni, Co and Mn is described. *Procedure*.—To the sample soln. add 5% aq. acetylacetone soln. (2 ml), adjust to pH 6 to 8 and dilute to about 50 ml. Use 10, 5 and 5 ml of chloroform to extract ferric acetylacetonate. Complete extraction of Fe is obtained, and only 0.1 to 0.01% of Co or Ni is extracted. For the separation from Mn a lower pH value ( $\approx 5$  to 6) is used.

D. C. ARMSWORTH

**2724. Spectrophotometric determination of iron as acetylacetonate by solvent extraction.** Masayuki Tabushi (Inst. for Chem. Res., Kyoto Univ., Kyoto). *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37** (4), 245-251.—*Procedure*.—To the sample soln. containing 10  $\mu$ g to 200  $\mu$ g of Fe add 2 ml of 5% aq. acetylacetone soln., adjust the pH to 6 to 8 (if the sample soln. does not contain a large amount of mineral acid, adjustment may be made by adding a few ml of 20% aq. ammonium acetate soln.) and dilute to  $\approx 50$  ml with  $H_2O$ . Shake the soln. with butyl acetate (20 ml), then dehydrate the organic phase with  $Na_2SO_4$  and measure the extinction at 440  $m\mu$  against a reagent blank or pure solvent. Beer's law is obeyed for 0.5 to 10 p.p.m. of Fe. Titanium, Cr and Bi interfere (owing to hydroxide formation), and  $UO_2^{2+}$ , Mn and large amounts of Cu give a positive error.

D. C. ARMSWORTH

**2725. Spectrophotometric determination of iron with quinolinic acid.** A. K. Majumdar and S. P. Bag (Jadavpur Univ., Calcutta, India). *Anal. Chim. Acta*, 1959, **21** (4), 324-330.—Quinolinic acid forms a 2:1 complex with  $Fe^{2+}$  at pH  $\approx 6$ . Its absorption max. is at 420  $m\mu$  and its instability const. is  $1.7 \times 10^{-3}$ . In the presence of KCN a 1:1 complex is formed at pH 9, which has an absorption max. at 440  $m\mu$ , a molar extinction coeff. of 2946 and an instability const. of  $2.73 \times 10^{-3}$ . When formed in the presence of hydroxyammonium chloride, this latter complex is suitable for the photometric determination of Fe in the optimum concn. range of 4 to 16 p.p.m. Beer's law is obeyed, and the relative error per 1% absolute photometric error is 2.94%. Fifteen common cations interfere when present in concn. ranging from 30 to 200 p.p.m. Silver, alkali metals and most common anions are without effect.

H. N. S.

**2726. Determination of iron in oxides. II. Comparison and selection of methods. [Iodimetric methods.]** L. Balabanoff K. (Lab. de Metalurgia, Univ. Concepción). *Bol. Soc. Chil. Quím.*, 1959, **9** (1), 24-28.—The precision of five iodimetric methods tested is inferior to that of the cerimetric method previously described (cf. *Anal. Abstr.*, 1960, **7**, 523). The initial addition of  $F^-$  to complex  $Fe^{3+}$  (Little and Hult, *J. Ind. Eng. Chem.*, 1920, **12**, 269) noticeably retards the oxidation of iodine by soln. of  $Cr_2O_3^{2-}$  and  $BrO_3^-$ . The method of Hammock and Swift (*Anal. Chem.*, 1953, **25**, 1113) is suitable for the precise routine determination of  $Fe^{3+}$ . For the determination of total Fe, a combination method is proposed; CuI and an excess of KI are added to the mixture of  $Fe^{2+}$  and  $Fe^{3+}$  in dil. HCl, and the liberated iodine is titrated with  $Na_2S_2O_3$  soln. to determine  $Fe^{2+}$ . The total Fe, now in the ferrous state, is oxidised by a measured excess of standard KBr -  $KBrO_3$  soln., the  $Fe^{3+}$  are complexed with

$NH_4F$  and the iodine liberated by the excess of oxidant is back-titrated with  $Na_2S_2O_3$  soln.

E. C. APLING

**2727. Determination of bivalent iron in the presence of  $Mn_2O_3$ ,  $Mn_2O_4$  and  $MnO_2$ .** J. Babčan (Inst. Mineral Raw Materials, Kutná Hora, Czechoslovakia). *Hutn. Listy*, 1959, **14** (9), 805-807.—The original Bregvadze method (*Sobshch. Akad. Nauk Grus. SSR*, 1954, **15**, 591) was revised and a modified procedure developed. *Procedures*: (i)  $Fe^{II}$  in the presence of  $MnO_2$ .—To the sample (0.3 to 0.5 g) add 0.2 N oxalic acid (20 ml), Reinhardt - Zimmermann soln. (2 ml) and  $H_2SO_4$  (1:4) (5 ml), close the flask with a stopper carrying a Bunsen valve and dissolve the contents by heating on a water bath. Add  $H_2SO_4$  (1:4) (40 ml) and conc.  $H_2PO_4$  (5 ml) and complete the dissolution on a sand bath. Cool to  $-7^\circ$  and titrate with 0.05 N  $KMnO_4$  (diphenylamine as indicator). (ii)  $MnO_2$  in the presence of  $Fe^{II}$ .—To the sample (0.3 to 0.5 g) add  $H_2SO_4$  (1:4) (50 ml), conc.  $H_2PO_4$  (5 ml) and 0.05 N  $(NH_4)_2SO_4 \cdot FeSO_4$  (20 ml), and heat on a water bath to dissolve the sample. Titrate the excess of  $(NH_4)_2SO_4 \cdot FeSO_4$  with 0.05 N  $KMnO_4$ . The same procedures can be used for the determination of  $Fe^{II}$  in the presence of  $Mn_2O_3$  and  $Mn_2O_4$  and of  $Mn_2O_3$  and  $Mn_2O_4$  in the presence of  $Fe^{II}$ . The accuracy of the method is discussed.

J. ŽYKA

**2728. Determination of ferrous iron in samples containing metallic and ferric iron.** Akira Kondo and Yoshitaro Fuke (Fac. of Engng, Ehime Univ., Niijima). *J. Japan Inst. Metals, Sendai*, 1958, **22** (6), 286-290.—For the removal of the mercury produced by the action of  $HgCl_2$  on metallic iron, the use of iodine soln. (3 to 5% of iodine in 10 to 30% KI soln.) is advocated. Large drops of mercury react with iodine very slowly but are removed easily by filtration. The sample is first treated with aq.  $HgCl_2$  soln. and filtered; the residue is treated with 5% iodine soln. in 20% KI soln. (30 ml) and filtered without suction from any remaining large drops of mercury. The residue is washed with 3% KI soln. until the washings become colourless, and is then acidified, and the  $Fe^{2+}$  are titrated with  $KMnO_4$  by the usual method.

K. SAITO

**2729. Determination of iron in its three states. Application to the complete analysis of iron sponge and to the determination of metallic iron in slags.** F. Marion and J. Aubry (Fac. des Sciences, Univ., Lille, France). *Chim. Anal.*, 1959, **41** (10), 401-407.—Ammonium argentothiocyanate soln. buffered at pH 4.5 to 4.6 is a reagent that preferentially dissolves Fe in the presence of iron oxides, according to the equation  $-2(NH_4)_2[Ag(SCN)] + Fe = (NH_4)_4[Fe(SCN)_6] + 2NH_4SCN + 2Ag$ . After filtration, the  $SCN^-$  are removed with  $Hg(NO_3)_2$  soln., and the soln. is again filtered. The Fe is then titrated with  $Ce^{IV}$  and ferroin. The Ag is dissolved from the oxide residue in the filter crucible by a Br - KBr - Na acetate soln. at  $80^\circ$ . The iron oxides are then dissolved in HCl (1:1) and  $Fe^{II}$  and  $Fe^{III}$  are determined cerimetrically. The procedure is suitable for the analysis of iron sponge, and for the determination of Fe in strongly basic slags. If Cu or copper oxides are present, then the reagent must contain KSCN in place of  $NH_4SCN$ . In the presence of Mn or Mg, the determination of Fe is valid only when the ratios of Mn to Fe and Mg to Fe are  $< 0.5$  and  $< 0.3$ , respectively.

J. H. WATON



2730. 2:4:6-Tri-(2-pyridyl)-sym-triazine as a reagent for iron. Determination of iron in limestone, silicates and refractories. P. F. Collins, H. Diehl and G. F. Smith (Dept. of Chem., Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1862-1867.—In acid soln. (pH 2.3 to 7),  $\text{Fe}^{2+}$  react with 2:4:6-tri-(2-pyridyl)-sym-triazine (I) to form the intensely violet-coloured  $\text{Fe}(\text{I})_3^{2+}$  (mol. extinction 22,600 at 593  $\mu$ ). In the presence of  $\text{ClO}_4^-$ , the complex may be quant. extracted into nitrobenzene within the pH range 3 to 7 with a slightly enhanced sensitivity (mol. extinction 24,100 at 595  $\mu$ ). The extinction of the organic extract is less dependent on pH than that of the unextracted soln., which is constant only within the pH range 3.5 to 5. Bivalent Cu (> 2.5 p.p.m.),  $\text{Co}^{II}$  (> 2.5 p.p.m.),  $\text{Ni}^{II}$  (> 5 p.p.m.),  $\text{Cr}^{III}$ , Ag,  $\text{Hg}^{II}$ ,  $\text{Bi}^{III}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{CN}^-$ ,  $\text{C}_2\text{O}_4^{2-}$  and  $\text{NO}_3^-$  interfere. Rock samples were decomposed by fusion with  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7$  (1:1) in silver crucibles, and any dissolved silver was subsequently separated as  $\text{AgCl}$  before photometric determination of Fe. The reagent is claimed to be simple to prepare, and the ready extractability of the  $\text{Fe}^{2+}$  complex is a major advantage.

T. R. ANDREW

2731. Utilisation of ternary and ion-association complexes in chemical analysis. I. Selective extraction and colorimetric determination of traces of iron as "ferroin iodide." F. Vydra and R. Přibil (Chem. Inst., Acad. Sci., Praha, Czechoslovakia). *Talanta*, 1959, **3** (1), 72-80.—Interference by Ag, Hg, Cu, Cd and Co in the determination of  $\text{Fe}^{II}$  by 1:10-phenanthroline (I) is avoided by forming the complex  $\text{Fe}^{II}(\text{I})_3$  in the presence of aq. EDTA soln. and  $\text{CHCl}_3$ , when it passes quant. into the  $\text{CHCl}_3$  at a pH between 3 and 10. The complexes with Br and Cl are not extracted. The extracted  $\text{Fe}^{II}$  is determined spectrophotometrically at 510 to 515  $\mu$  (the absorption max. of the complex). The accuracy for 1 to 2.5  $\mu$ g per ml of  $\text{Fe}^{II}$  is within  $\pm 1\%$ ;  $\text{Fe}^{II}$  can be determined in the presence of Ni, Zn, Mn, Cr, Al and Ti (2 to 3 mg), Co (4 mg), Cu (8 mg), Zr (9 mg), Cd (11 mg) and U, Pb, Th, and Bi (20 to 30 mg).

J. P. STERN

2732. Comparison of various methods for the determination of manganese in steel, iron and ferromanganese. H. Pohl. *Materialprüf.*, 1959, **1**, 54-57.—The official method in Germany for the determination of Mn is the Volhard-Wolff method which gives results that are 0.01 to 0.03% high. The acceptance of a method in which the  $\text{Mn}^{II}$  forms a  $\text{Mn}^{III}$ -pyrophosphate complex at pH 6.5, with potentiometric end-point determination, is suggested. This method gives results that are in excellent agreement with those of methods adopted officially in other countries.

J. IRON ST. INST. ABSTR.

2733. Spectrographic analysis of solutions with spark excitation. Applications to low-alloy steel, copper alloys and slag. A. Larsson (Metallographic Inst., Stockholm, Sweden). *Jernkontor. Ann.*, 1959, **143** (8), 508-522.—The principal advantages of the solution technique in spectrographic analysis are mentioned. Several ways to excite and to impregnate carbon electrodes with steel soln. were tried. The quality of the carbon has great influence on the results. Better reproducibility was obtained with copper electrodes (for steel and slag) and silver electrodes (for copper alloys) in combination with an adhesive solution technique (Pfeilsticker, *Spectrochim. Acta*, 1950, **4**, 100). In steel samples, 4% of Ni, 2% of Cr, 1% of Mn, 0.5% of Mo and 0.5% of V

can be determined with a reproducibility of  $\pm 2\%$ . In copper alloys, 2% to 11% of Sn, Pb and Zn can be determined with the same reproducibility. In slag,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{CaO}$  and  $\text{MgO}$  can be determined in a sample wt. of only 0.2 mg. Details of procedures are given for steel, copper alloys and slag.

B. RÖNNHOLM

2734. The solution spectral analysis of oxide inclusions in steel. S. Meyer and O. G. Koch (Neunkircher Eisenwerk A.-G., Neunkirchen/Saar, Germany). *Spectrochim. Acta*, 1959, (8), 549-556.—A spectrographic micro-solution technique is described for the determination of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{CuO}$  contents in steel oxide inclusions. A micro sample,  $\approx 100$  to 500  $\mu$ , is fused with  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$ - $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  (3:3:4), and dissolved with a soln. containing 1% of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 1% of citric acid and 2-75 N in HCl. Cobalt is the internal standard. The final soln. vol. is 200  $\mu$ l (sample wt. 150 to 300  $\mu$ g) or 100  $\mu$ l (sample wt. 100 to 150  $\mu$ g). An aliquot (20  $\mu$ l) is pipetted on to a pre-sparked, pre-heated graphite electrode and sparked. The coeff. of variation of a single result is  $\pm 5.5\%$  and time of analysis is  $\approx 1$  hr.

G. P. MITCHELL

2735. The extraction of transition metals as polyglycol-oxonium complexes and the detection of cobalt as a poly(oxy)ethylene glycol-thiocyanate complex. M. Ziegler (Inorg. Chem. Inst., Univ., Göttingen, Germany). *Z. anal. Chem.*, 1959, **171** (2), 111-114.—The colour and extractability of the complexes formed with polyoxyethylene glycols and metal iodides and thiocyanates are given. Dichloro-, dibromo- or di-iodo-methane is favoured as extractant, chloroform being useless. Coloured complexes are given by  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$  and  $\text{Hg}^{2+}$ . The test for Co is as follows. Shake the test soln. (pH  $\approx 3$ ) with 5 drops of 50% aq. KSCN soln. and 5 to 10 drops of 50% aq. polyoxyethylene glycol 400 soln. Add 0.2 g to 0.5 g of KF and shake with a little dichloromethane. A blue colour in the organic layer indicates Co; 0.5  $\mu$ g of Co at a concn. of  $1$  in  $4 \times 10^4$  can be detected;  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  do not interfere. H. M.

2736. Macro- and micro-determination of traces of cobalt. II. Separation of traces of cobalt by extraction with dithizone. D. Monnier, W. Haerdi, J. Vogel and P. E. Wenger (Lab. de Chim. Minérale, Chim. Anal. et Microchim., Univ. Genève). *Helv. Chim. Acta*, 1959, **42** (6), 1846-1854 (in French).—The recovery of trace amounts of Co ( $1 \times 10^{-4}$  to  $1 \times 10^{-6}$  g) from aq. soln. with dithizone was studied by means of  $^{60}\text{Co}$ . Satisfactory recoveries were obtained by extraction with dithizone in diethyl ether in the presence of a citrate buffer soln. at pH 8. A procedure is given for the decomposition of the extracted complex. The residual Co is then determined colorimetrically or by polarography.

A. G. COOPER

2737. Spectrophotometric determination of cobalt after extraction of the thiocyanate complex with acetylacetone. W. B. Brown and J. F. Steinbach (Dept. of Chem., Univ. of Kentucky, Lexington, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1805-1806.—Extraction with acetylacetone at pH 4 removes interfering cations; subsequent addition of  $\text{NaSCN}$  soln. and extraction of the cobalt thiocyanate complex with more acetylacetone before measurement of the extinction at 625  $\mu$  serves to determine Co. The method has been applied to the analysis

of steel. The extinction of the acetylacetone soln. of the cobalt thiocyanate complex remains unchanged for 10 days.

T. R. ANDREW

**2738. Determination of cobalt by radiometric titration with potassium ferrocyanide.** D. I. Eristavi, F. I. Brouchek and T. A. Tsitsivadze (S. M. Kirov Georgian Polytech. Inst., Tbilisi). *Zhur. Anal. Khim.*, 1959, **14** (5), 631-633.—By using the radioactive isotope  $^{60}\text{Co}$ , it is shown that the ppt. formed by the reaction of  $\text{CoSO}_4$  with  $\text{K}_4\text{Fe}(\text{CN})_6$  has the composition  $[\text{Co}_2\text{Fe}(\text{CN})_6]_x \cdot \text{K}_y\text{Fe}(\text{CN})_6$  or  $\text{K}_x\text{Co}_{10}[\text{Fe}(\text{CN})_6]_x$ . This reaction may be used for the radiometric titration of small amounts of Co with  $\text{K}_4\text{Fe}(\text{CN})_6$ ; during the earlier part of the titration the activity of the centrifuged soln. is inversely proportional to the amount of ferrocyanide added, and this section of the titration curve can be extrapolated to zero activity to find the end-point; further addition of ferrocyanide causes a deviation from rectilinearity, due to the noticeable solubility of the ppt.

C. D. KOPKIN

**2739. Micro-titration of rhodium with sodium pentamethylenedithiocarbamate.** N. K. Pshenitsyn and N. V. Fedorenko (N. S. Kurnakov Inst. of Gen. and Inorg. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 588-591.—Add 1 ml of an aq. soln. of NaCl (0.3 mg per ml) (to prevent hydrolysis) to a soln. of a complex rhodium chloride (0.003 to 0.3 mg of Rh), evaporate to dryness three or four times to remove excess of HCl, dissolving in hot water each time, wash the dry residue into a test-tube (110 mm  $\times$  20 mm) with 2.5 ml of 0.90 N HCl, add 0.5 ml of  $M$   $\text{SnCl}_2$  in 0.90 N HCl, and place the stoppered tube in boiling water for 10 min. Cool, add 10 ml of dichloroethane and titrate with an aq. soln. of sodium pentamethylenedithiocarbamate in small portions (0.05 or 0.1 ml), shaking the tube after each addition, till the aq. layer is decolorised. The reagent soln. is preferably of such a concn. that the vol. used does not exceed 1 ml; it is stable for 5 or 6 days. The soln. of  $\text{SnCl}_2$  should be clear. All the other platinum metals interfere.

C. D. KOPKIN

**2740. Extraction of palladium with organic solvents. I. The use of the labelled-atom method for the extraction of palladium(II) as reineckate.** V. Voicu and I. Dema (Inst. Atom. Phys., Bucharest). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (3), 431-439.—The extraction of Pd reineckate with ethyl methyl ketone (I) has been followed by means of palladium containing  $^{106}\text{Pd}$ , produced by neutron activation. *Procedure*—A soln. of  $\text{Pd}^{2+}$  (45 to 75  $\mu\text{g}$ ) is made 0.1 to 0.75 N in HCl and treated with 1 ml of a 1% aq. soln. of ammonium reineckate. The mixture is diluted to 10 ml and shaken for 2 min. with 10 ml of I. The activity of the organic layer is then measured. It is shown that from  $10^{-4}$  to  $10^{-5}$  g of Pd can be determined in the presence of  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Rh}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{In}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Be}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ga}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{ZrO}^{2+}$  and  $\text{Th}^{4+}$ ;  $\text{Au}^+$ ,  $\text{Au}^{3+}$ ,  $\text{Pt}^{4+}$ ,  $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Hg}_2^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ti}^{3+}$  and  $\text{Cd}^{2+}$ , which give ppt. with ammonium reineckate, must be absent. The error is  $\pm 1\%$ .

H. SHER

**2741. Amperometric determination of palladium with 2-(*o*-hydroxyphenyl)benzoxazole.** R. F. Wilson, L. J. Baye and J. James (Dept. of Chemistry, Texas Southern Univ., Houston, Tex., U.S.A.). *Z. anal. Chem.*, 1959, **171** (2), 103-106 (in English).—The Pd soln. in 2 M acetic acid - Na acetate buffer

(1:1, 10 ml) and  $\text{HClO}_4$  (20 ml) to white fumes, containing a little gelatin is freed from oxygen by bubbling with purified nitrogen in one arm of an H-type cell. The reference electrode (S.C.E.) is contained in the other arm, the two soln. being separated by a KCl - agar sintered glass disc. Measurement of current is made at - 0.5 V after adding a little titrant, stirring with nitrogen and allowing the soln. to stand for 2 min. The current readings are plotted against vol. of titrant added and the vol. of titrant used is found by extrapolation. Only Ir was found to interfere. The titrant is a 0.1 M soln. of 2-(*o*-hydroxyphenyl)benzoxazole in acetic acid.

H. M.

**2742. Spectrophotometric determination of palladium with 4-methylcyclohexane-1:2-dione dioxime.** C. V. Banks and R. V. Smith (Iowa State Coll., Ames, U.S.A.). *Anal. Chim. Acta*, 1959, **21** (4), 308-311.—*Procedure*—Adjust the soln., containing 2.5 to 250  $\mu\text{g}$  of Pd, to a pH value between 0.7 and 5.0 by adding a HCl - KCl buffer (5.3 ml of 0.2 N HCl and 25 ml of 0.2 N KCl diluted to 100 ml), add 1 ml of saturated aq. 4-methylcyclohexane-1:2-dione dioxime and set aside for 1 hr. Extract with three 7-ml portions of  $\text{CHCl}_3$ , dry the extract with  $\text{Na}_2\text{SO}_4$  and determine the extinction at 280  $\mu\text{m}$  in a 1-cm cell. The following ions interfere— $\text{Ru}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , but microgram quantities of  $\text{Cu}^{2+}$  are masked with thioglycolic acid,  $\text{Co}^{3+}$  are converted into the hexacyanocobaltic complex, and  $\text{Fe}^{2+}$  are oxidised to  $\text{Fe}^{3+}$  which are masked with  $\text{F}^-$ .

H. N. S.

**2743. Rapid analysis of magnesia clinker for basic refractories by the EDTA method.** Takeru Honjo, Hiroshi Goto and Yoshinori Watabe (Refractory Works, Japan Steel and Tube Co., Oogimachi, Kawasaki, Kanagawa-ken). *J. Ceram. Ass. Japan*, 1959, **67** (8), 275-279.—EDTA titration was applied to the determination of Fe, Al, Ca and Mg in magnesia clinker after decomposition with HCl and  $\text{HClO}_4$  and removal of  $\text{SiO}_2$ . *Procedure for Fe and Al*—To a 50-ml aliquot of the soln. add ammonium acetate soln. (50%, 10 ml) and salicylic acid (2%) in methanol (3 ml), adjust to pH 3 and titrate the Fe with 0.01 M EDTA (disodium salt). Boil the colourless soln., add copper - PAN indicator (2% in 50% isoamyl alcohol, 3 drops) and again titrate with EDTA soln. until the yellow colour remains unchanged on boiling for 30 sec. This gives the Al. *Procedure for Ca*—Add triethanolamine soln. (1:1, 2 ml) to a second 50-ml aliquot, adjust the pH to 12.5, add 3-hydroxy-4-(2-hydroxy-4-sulpho-1-naphthylazo)-2-naphthoic acid as indicator and titrate with EDTA soln. *Procedure for Ca and Mg*—Add hydroxyammonium chloride soln. (1.5%, 2 ml), KCN soln. (5%, 1 ml) and triethanolamine soln. (1:1, 2 ml) to a third aliquot, adjust the pH to 10 and titrate with EDTA soln., with Eriochrome black T as indicator.

K. SAITO

**2744. Studies on the chemical analysis of basic slag. I. Determination of silica, total iron, alumina, manganese oxide, calcium oxide and magnesia.** Shigeo Wakamatsu (Toto Seiko Co., Minami-sunamachi, Koto-ku, Tokyo). *J. Iron St. Inst. Japan*, 1959, **45** (7), 717-722.—The sample is decomposed with HCl, treated with  $\text{HClO}_4$  and the  $\text{SiO}_2$  determined gravimetrically, Cr ( $> 10\%$ ) being removed as  $\text{CrO}_2\text{Cl}_2$ . Total Fe, Al, Mn, Ca and Mg are successively titrated with EDTA (disodium salt). The time taken for a determination is  $< 3$  hr. *Procedure*—Heat the sample (0.5 g) with HC

dissolve in HCl (1:1, 5 ml), filter and determine the  $\text{SiO}_2$  as usual. Make up the filtrate and washings to 250 ml, mix a 50-ml portion with water (40 ml) and salicylic acid (I) (10% in ethanol, 0.5 ml), bring to pH 2.0 with ammonium acetate soln. (II) and titrate with 0.0125 M EDTA (disodium salt) (for Fe). Add  $\text{CuSO}_4$  (0.0125 M, 0.10 ml) to the product, bring to pH 3 with II, boil, add 1-(2-pyridylazo)-2-naphthol (III) (0.1% in methanol, 3 drops) and EDTA (disodium salt) soln. (1 ml in excess) and titrate with 0.0125 M  $\text{CuSO}_4$  (for Al). Heat the product to 60°, bring to pH 4.5, add EDTA (disodium salt) soln. (2 ml in excess) and titrate with  $\text{CuSO}_4$  soln. after 10 min. (for Mn). Dilute the product to 250 ml and adjust a 50 to 100-ml portion to pH 10. Add EDTA (disodium salt) soln. to the red soln. until it becomes yellow, then 2 ml in excess. Add III (3 drops) and titrate with  $\text{CuSO}_4$  soln. (for Ca + Mg). Add saturated ammonium oxalate soln. (20 ml) to another 100-ml portion to precipitate Ca, filter, and titrate the Mg in the filtrate by the usual method.

**II. Determination of iron(II), iron(III) and titanium.** Shigeo Wakamatsu. *Ibid.*, 1959, 45 (8), 808-812.—Whilst  $\text{Fe}^{III}$  reacts with EDTA at pH 2,  $\text{Fe}^{II}$  does so at a much higher pH. Titanium is determined photometrically (at 380 m $\mu$ ) with I at pH 4 to 5, the Fe Cu, Cr and V being masked with EDTA. There is no interference from Al, Mn, Ca, Mg, Pb, Th, Mo or Nb. *Procedure*—Dissolve the sample (0.1 to 0.2 g) in HCl (1:1, 15 ml) in a current of  $\text{CO}_2$ , evaporate to < 10 ml, cool, add water (100 ml) and I soln. (0.5 ml), adjust to pH 2.0 with II and titrate with EDTA (0.0125 M) (for  $\text{Fe}^{III}$ ). Add  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  soln. (20%, 10 ml) to the product and titrate further with the EDTA until the purple colour formed is discharged (for  $\text{Fe}^{II}$ ). To a 25-ml portion of the filtrate from the pptn. of  $\text{SiO}_2$  (see Part I) add HCl (1:1, 10 ml), water (15 ml), I soln. (10 ml) and the II soln. (10 ml), adjust the pH to 2 to 3, add EDTA until the colour is discharged, then a further 5 ml, adjust to pH 4 to 5 and dilute to 100 ml for photometry. To another 25-ml portion of the filtrate add the same amounts of the reagents except I and use the product as reference soln.

**III. Determination of sulphur.** Shigeo Wakamatsu. *Ibid.*, 1959, 45 (10), 1164-1168.—For the determination of S in samples free from F, the ordinary combustion method suffices. For those containing F, the outflowing gas is collected in an absorbing soln. consisting of 20 ml of 0.1%  $\text{H}_2\text{O}_2$  and 5 ml of 0.009%  $\text{CuCl}_2$ . The  $\text{SO}_2$  is absorbed and the soln. is mixed with ethanol (20 ml), neutralised with 0.1 N KOH to methyl red, mixed with Na rhodizonate soln. (0.05%, 1 ml) and an excess of 0.04 M  $\text{BaCl}_2$  and the excess of  $\text{Ba}^{++}$  is back-titrated with 0.04 M  $(\text{NH}_4)_2\text{SO}_4$ . For a large amount of S (> 0.2%), the sample (2 g) is fused with  $\text{Na}_2\text{O}_2$  (20 g) and the S determined photometrically with  $\text{Fe}^{III}$  in  $\text{HClO}_4$  (*cf. Anal. Abstr.*, 1960, 7, 1719).

K. SARRO

See also Abstracts—2593,  $\text{K}_2\text{CS}_3$  as substitute for  $\text{H}_2\text{S}$ . 2594, 2602, Indicators for Ca and Mg titrations. 2603, Determination of Cu. 2750, Determination of  $\text{SO}_4^{2-}$ . 2759, Determination of  $\text{O}_2$ . 2779, Urea in black chromium plating bath. 3070, Boron in plants. 3011, Trace elements in plants. 3018, Potassium in fertilisers. 3021, Instrumentation in the foundry lab. 3034, Extraction of metal chelates. 3037, Detection of cations on paper chromatograms. 3060, Gas analysis by h.f. discharge. 3079, Determination of F-. 3099, Measurement of  $^{14}\text{C}$ .

## 3.—ORGANIC ANALYSIS

*Determination of elements and radicals and of organic compounds not included in other sections. Organic industrial products, including petroleum and its products, fuels, detergents, volatile oils, cosmetics, dyestuffs, fibres, plastics, resins, paints, elastomers, leather, explosives.*

**2745. Electrical ignition in the Schöniger oxygen flask method.** A. J. Martin and H. Deveraux (E. I. du Pont de Nemours & Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, 31 (11), 1932.—In the conventional procedure the filter-paper is ignited by an open flame, after which the adapter is inserted quickly into the flask containing oxygen. The adapter described permits the electrical ignition of the sample and filter-paper and the whole operation can be carried out in a closed system, which is more suitable for the handling of thermally unstable materials. G. P. COOK

**2746. Radiometric absorption analysis. I. Elementary analysis with a methane-flow tube counter as radiation detector.** L. Wiesner (Inst. Erdöl-forschung, Hannover, Germany). *Brennstoffchemie*, 1959, 40 (9), 273-278.—If the rates of transmission of radiation of a number ( $n$ ) of elements exposed to radiations of ( $n - 1$ ) different energy levels are known, then a compound containing some or all of these elements can be completely analysed, since its absorptive power for each radiation is  $S = \Sigma(E_m S_m)$ , where  $E_m$  is the proportion by weight of the  $m^{\text{th}}$  element of effective cross-section  $S_m$ ;  $E$  of the last element is obtained by difference. Suitable radioactive sources are  $^{56}\text{Fe}$ ,  $^3\text{H}$ ,  $^{106}\text{Cd}$ ,  $^{90}\text{Sr} + ^{90}\text{Y}$ ,  $^{60}\text{Co}$  and  $^{241}\text{Am}$ . The methane-flow proportional counter is preferred to the Geiger-Müller type because of its shorter dead period after each impulse. The rates of transmission of the sample and of a standard substance (heptane) are compared, the ratio thus found being unaffected by decay of the source. Calibration curves of ratio vs. concn. of element are given for S, Cl, H, Pb and iodine. Each element slightly affects the absorption of the others, and corrections for the mutual interferences of H, N, O, P, S, Cl, Pb and iodine are tabulated. The apparatus and method of calculation are described. The method has been applied successfully to routine determinations of S in petroleum products.

A. R. PEARSON

**2747. Quantitative determination of halogens in organic compounds.** A. A. Bugorkova-Zelenetskaya, E. N. Novikova and L. N. Petrova (All-Union Sci. Res. Inst. of Synthetic and Natural Perfumes, Moscow). *Zhur. Anal. Khim.*, 1959, 14 (5), 625-627.—Primary chlorides containing an active group ( $-\text{C}-\text{C}-$ , benzene ring,  $-\text{COOH}$ ) in the  $\alpha$ -position (benzyl chloride, cumyl chloride,  $\beta$ -phenylallyl chloride, allyl chloride, methallyl chloride, chloroacetic acid, 4-chloro-2-methylbut-2-ene, geranyl chloride) react quant. with KI in boiling anhyd. acetone; the resulting KCl is filtered off, washed with anhyd. acetone till no reaction for  $\text{I}^-$  is obtained (tested with  $\text{AgNO}_3$ ), and dissolved in a small vol. of water, and  $\text{Cl}^-$  are determined by Mohr's method. Benzylidene chloride, cumylylidene chloride, isobutyl chloride and terpenyl chloride do not react. Mixtures of benzyl and benzylidene chlorides and cumyl and cumylylidene chlorides can be analysed



by determining the former constituents by the method described, and determining total chlorine by the earlier method (*Anal. Abstr.*, 1960, 7, 558), but with 0.5 N alkali in ethanediol-water-ethanol (2:1:1). By the described method geranyl chloride can be determined in the presence of linalyl chloride and terpenyl chloride. C. D. KOPKIN

**2748. The applicability of different tube packings in the determination of nitrogen.** G. Kainz and L. Hainberger (II Chem. Inst., Univ., Wien). *Z. anal. Chem.*, 1959, **169** (6), 406-410.—If methane from the combustion of organic matter is not completely oxidised, it passes on into the nitrometer and causes errors in the determination of N. Several metal oxides were tested as tube packings by passing a known amount of methane over each at different temp. and measuring the vol. of unburnt gas;  $\text{CO}_2$  (4 ml per min.) was used as a carrier gas. The temp. required for complete combustion ranged from 420° ( $\text{MnO}_2$ ) to 850° (NiO) and was correlated with the partial pressure of O of the oxides. The best packing was  $\text{Co}_3\text{O}_4$  which quant. oxidised methane at 660° and had a working range from about 630° to 850°.

P. D. PARR-RICHARD

**2749. Organic quantitative analysis. XXI. New method for nitrogen determination with cobaltocobaltic oxide as combustion catalyst.** M. Večeřa and L. Synek (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, **24** (10), 3402-3406 (in German).—The substance is burnt in a stream of  $\text{CO}_2$  in the presence of  $\text{Co}_3\text{O}_4$  and of electrolytically generated O. The excess of O is retained on a layer of copper. The method was tested on difficultly combustible substances, including polymers. *Procedure*.—Insert the sample (2 to 5 mg) into the combustion tube, switch on the movable electric furnace and the electrolyser and adjust the flow-rate of the  $\text{CO}_2$  to 2 bubbles per min. Burn the sample in the usual way within 8 to 10 min. During the 10th and the 11th min. increase the velocity of the  $\text{CO}_2$  stream to 4 bubbles per min. During the 12th and 13th min. stop the  $\text{CO}_2$ . After 15 min. read the vol. of N, and subtract 1.1% of the observed vol. and the vol. of the blank (0.002 to 0.005 ml) before calculation. The preparation of  $\text{Co}_3\text{O}_4$  on an asbestos base is described in a previous communication (Synek and Večeřa, *Anal. Abstr.*, 1958, 5, 851). J. ZÝKA

**2750. Volumetric micro-determination of organically bound sulphur and organic and inorganic sulphates.** R. N. Boos (Merck & Co. Inc., Rahway, New Jersey, U.S.A.). *Analyst*, 1959, **84**, 633-635.—The sample is burned in an atmosphere of O in the presence of  $\text{H}_2\text{O}_2$  in a Schöniger apparatus. After complete combustion the liquid is treated with  $\text{BaCl}_2$  soln. (0.005 M) and is evaporated to dryness to remove  $\text{H}_2\text{O}_2$ . It is then treated with water and specified amounts of ammonium acetate soln., a mixed soln. of mercuric acetate and EDTA (disodium salt), and aq.  $\text{NH}_3$ , and the excess of  $\text{BaCl}_2$  is titrated potentiometrically with EDTA soln. Quoted results with organic compounds indicate satisfactory accuracy. The method could be used for determining inorganic sulphates, but metals forming chelates with EDTA would have to be removed by passage through an ion-exchange column before the  $\text{BaCl}_2$  is added. A. O. JONES

**2751. Studies on organic micro-analyses. XVIII. Basic principles of the Clauson-Kaas micro-hydrogenation apparatus.** Keiichiro Hozumi (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1959, **79** (2), 131-135.—The quantitative micro-hydrogenation apparatus, reported by Clauson-Kaas and Limborg (*Acta Chem. Scand.*, 1947, **1**, 884), was examined. The slow response of the manometer scale after refilling the reaction vessel with H appears to be due to the asymmetric structure of the vessel and the compensator. It is therefore better to introduce H previously saturated with the solvent and to reduce the volume of the reaction vessel in order to stabilise the pressure quickly. The compensator is rendered unnecessary by these improvements if the reaction vessel is immersed in a thermostat.

**XIX. Modified micro-hydrogenation apparatus and a rapid method of calculation.** Keiichiro Hozumi. *Ibid.*, 1959, **79** (2), 135-139.—The apparatus described in Part XVIII was used. The pressure in the reaction vessel reaches equilibrium within 20 to 30 min. after sweeping with H. The apparatus is smaller and more convenient for washing and drying than the original one. The Clauson-Kaas calculation formula is based on ideal conditions and is not suitable for practical use. A new formula and calculation table are presented.

**XXI. An improved method for determining alkoxy groups by the use of porous silver granules and absorption tube.** Keiichiro Hozumi. *Ibid.*, 1959, **79** (2), 237-241.—A sample containing alkoxy groups is distilled with the reaction mixture of Kirsten and Ehrlich-Rogozinsky (*Anal. Abstr.*, 1955, 2, 3080) in a modified Zeisel apparatus for 40 min. for methoxyl and 60 min. for ethoxyl in a current of air (10 ml per min.). The alkyl iodide is passed through 5% potassium antimonyl tartrate soln. and then through an absorption tube of translucent quartz, containing porous silver granules (2 g) at 400° to 500°. The alkyl iodide is thus decomposed to iodine, which is absorbed by the silver, and the increase in weight of the absorption tube is measured 15 min. after the completion of the distillation.

S. NATORI

**2752. Problems of analytical determination of -C:C- bonds.** B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague). *Chem. Listy*, 1959, **53** (10), 997-1028.—A review with 373 references. The following methods are discussed—(i) chemical methods (hydrogenation, methods based on the addition of halogens, addition of mercuric salts, determination with peroxy acids, oxidation with  $\text{KMnO}_4$  and  $\text{KIO}_4$ , methods of electrophilic and nucleophilic addition, determination of conjugated bonds), and (ii) physical methods (polarography and i.r. spectroscopy). J. ZÝKA

**2753. Detection and determination of peroxy groups.** H. Hartkamp (Inst. für Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck, Germany). *Angew. Chem.*, 1959, **71** (20) 651-652.—The method is based on the reaction of quinquivalent V in acid soln. with  $\text{H}_2\text{O}_2$  in the presence of pyridine-2:6-dicarboxylic acid (I). This reaction is specific for peroxy groups, and is as sensitive as the method for the detection of peroxide with  $\text{TiOSO}_4$ . The reagent (II) is prepared by evaporating equimolar soln. of  $\text{NH}_4\text{VO}_3$  and I. Filter-paper treated with an aq. soln. of II and dried is stable and can be used for the detection of peroxides; peroxides in liquids immiscible with water are extracted with I in acid soln. The



extinction of the orange peroxy compound is measured at 432 m $\mu$ . Beer's law is obeyed for concn. of  $\approx 0.7$  to 70  $\mu\text{g}$  of  $\text{H}_2\text{O}_2$  per ml.

B. B. BAUMINGER

**2754. Spectrophotometric study of olefin-metal ion co-ordinate covalent compounds.** P. Urone (R. A. Taft San. Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1768-1770.—Olefin-metal ion co-ordinate compounds were studied to determine whether spectrophotometric methods could be used to measure small amounts of olefins in air or gaseous mixtures. The reactions of ethylene, propylene and *cis*-but-2-ene with  $\text{Hg}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Cu}^+$  and platinum ions in various solvents were studied. Mercuric salts were the best co-ordinating agents, and methanol and glacial acetic acid soln. of  $\text{HgO}$  were chosen because of the greater solubility of the olefins in non-aqueous solvents. After reaction of the olefins with the  $\text{Hg}^{2+}$  soln., the decrease in extinction was measured. As little as 5  $\mu\text{g}$  of olefin can be determined. G. P. Cook

**2755. Determination of the structure of alkanes and naphthenes by infra-red spectroscopy.** Yu. P. Egorov, V. A. Shlyapochnikov and A. D. Petrov (N. D. Zelinskii Inst. of Org. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 617-624.—The numbers of  $-\text{CH}_3$ - and  $-\text{CH}_2$ - groups in branched-chain alkanes and naphthenic hydrocarbons can be found from the i.r. spectra at 2930 and 2965  $\text{cm}^{-1}$ , corresponding to antisymmetric vibrations of the C-H bonds. From a study of  $\text{C}_7$  to  $\text{C}_{24}$  branched alkanes and  $\text{C}_8$  to  $\text{C}_{20}$  naphthenic hydrocarbons, it is shown that the molar extinction coefficients for these bands are directly proportional to the number of  $-\text{CH}_3$ - and  $-\text{CH}_2$ - groups, respectively, and can be used to estimate the numbers of these groups, with an average error of  $< 0.5$  group. The bands are additive in their absorption, and the resulting spectrum can easily be analysed into its two components. C. D. KOPKIN

**2756. Determination of propadiene traces in propene.** E. Bua, P. Manaresi and L. Motta (Ist. Ricerche Idrocarburi, Ferrara, Italy). *Anal. Chem.*, 1959, **31** (11), 1910-1911.—Complete separation of traces of propadiene in a large excess of propene can be achieved by a column of 30%  $\text{AgNO}_3$  in ethanediol on firebrick. The precision (95% confidence limits) is  $\pm 15$  and  $\pm 3\%$  at the 5 and 2 p.p.m. levels, respectively, from 10 determinations at each level. With an enrichment technique  $< 1$  p.p.m. can be detected. G. P. Cook

**2757. Determination of organic halides with dispersed sodium.** R. L. Menville and W. W. Parker (Ethyl Corp., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1901-1902.—An appropriate sample containing 25 to 150 mg of halogen is dissolved in benzene (50 ml) and dispersed sodium (2 to 3 ml) is added. The mixture is then treated with isopropyl alcohol (10 to 15 drops) and the reaction is allowed to proceed for 5 min. Methanol is added to react with the excess of sodium and the soln. is acidified with  $\text{HNO}_3$ . The halogen content is determined by potentiometric titration with  $\text{AgNO}_3$  soln. The precision and accuracy of the method are  $99.8 \pm 1.5\%$ . G. P. Cook

**2758. Radio-gas-chromatography of neutron-irradiated alkyl halides and identification of recoil reaction products.** W. Herr, F. Schmidt and G. Stöcklin (Max-Planck-Inst. f. Chem., Mainz). *Z. anal. Chem.*, 1959, **170** (1), 301-310.—*n*-Propyl

bromide contained in quartz ampoules was irradiated with neutrons in a nuclear reactor. The products were identified by gas chromatography, with simultaneous counting of the  $^{82}\text{Br}$  activity. A device for breaking the ampoules within the inlet system is described. The effect of added aromatic amines was investigated. Unsaturated recoil reaction products containing  $^{82}\text{Br}$  are formed only in the presence of certain aromatic amines and with intensive irradiation. The addition of amines greatly increases the yield of labelled original compound. G. BURGER

**2759. Iodimetric micro-determination of organic oxidants and ozone. Resolution of mixtures by kinetic colorimetry.** B. E. Saltzman and N. Gilbert (U.S. Dept. of Health, Educ. and Welfare, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1914-1920.—A slow-reacting iodide reagent was added to the test soln., and measurements of the colour development were made at progressive time intervals, at 352 m $\mu$ , until max. colour was attained. The log of the undeveloped colour (max. extinction — the extinction at the given time) was plotted against the reaction time. Pure substances undergoing a single reaction with the reagent gave straight-line plots with characteristic slopes. Binary mixtures were resolved into the arithmetic sum of two straight lines, one for each component. This kinetic colorimetry was successfully applied to the determination of several oxidants. Studies of various iodide reagents for the determination of low concn. of  $\text{O}_3$  in air showed that the most precise and stable of those tested was 1% KI soln. in neutral phosphate buffer. The stoichiometry of this reagent for pure  $\text{O}_3$  in air was determined by another method, based on the conversion of the  $\text{O}_3$  into  $\text{NO}_2$ , and was found to be very close to  $\text{O}_3 = \text{I}_2$  in the range 2 to 80 p.p.m. G. P. Cook

**2760. Determination of small amounts of chloride in ethylene oxide.** J. G. Hanna and H. M. Schramm (General Aniline & Film Corp., Linden, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1821-1822.—Organic chloride is converted into inorganic chloride by treatment at  $0^\circ$  with NaOH soln. The ethylene oxide is removed by evaporation at  $100^\circ$  and the soln. is acidified with  $\text{HNO}_3$ . The chloride is then determined by the Volhard technique, and represents the sum of inorganic chloride plus loosely bound chlorine from 2-chloroethanol which may be present in the sample. The standard deviation is  $\pm 0.004\%$  at the 0.02% of chloride level, from 11 determinations by four operators; the mean recovery is 100%. G. P. Cook

**2761. Acid-catalysed acetylation of organic hydroxyl groups.** J. S. Fritz and G. H. Schenk (Iowa State Univ., Ames, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1808-1812.—Primary and secondary alcohols are determined by acetylation in ethyl acetate or pyridine soln., with  $\text{HClO}_4$  to catalyse the reaction. Alcohols soluble in ethyl acetate are completely acetylated within 5 min. at room temp. In pyridine a somewhat longer reaction time is required for secondary or hindered alcohols. The amount of alcohol present is calculated from the difference between the blank and sample titrations with NaOH soln. Analysis of about 30 alcohols, sugars and hydroperoxides gave results in the range 98 to 100%. Aldehydes interfere in both solvents; enols, imides, hydrazides and oximes are acetylated in varying degrees. In ethyl acetate, double bonds and furan rings interfere, but triple

bonds do not. Amines, phenols, thiols and some oximes are quantitatively acetylated.

G. P. COOK

**2762. Use of a new stationary liquid phase in gas-chromatography determination of alcohols in the presence of large amounts of water.** J. E. Zarembo and I. Lysyj (Central Research, Food Machinery and Chemical Corp., Princeton, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1833-1834.—A high-boiling mixture of primary amines, Armeen SD, has been used as the stationary phase on a 22-ft. column for the separation of alcohols and water (25 to 75%) on the basis of their polarity. The concn. of water and alcohols can be determined directly by integration of the areas under their respective peaks.

K. A. PROCTOR

**2763. Determination of trace amounts of inorganic chloride in ethanediol.** J. G. Hanna and J. Jura (General Aniline & Film Corp., Linden, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1820-1821.—A soln. of the sample in an alcohol e.g., *n*-heptanol or octan-2-ol, is titrated with  $\text{AgNO}_3$  soln., with a silver-modified calomel electrode system, which eliminates the need for a salt bridge. The standard deviation is  $\pm 0.03$  p.p.m. in the concn. range of 0.1 to 1.0 p.p.m.

G. P. COOK

**2764. Determination of mono-, di- and tri-ethylene glycols in mixtures by gas-liquid chromatography.** L. Ginsburg (General Aniline & Film Corp., Linden, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1822-1824.—Up to 2% each of mono- and tri-ethylene glycols in diethylene glycol and up to 8% of diethylene glycol in ethylene glycol can be determined at 200° on a 2-metre column of Apiezon L. Peak-height measurement is used for calibration, and results obtained are comparable in accuracy with those of conventional methods.

K. A. PROCTOR

**2765. Determination of penta-substituted glycerols by periodic oxidation.** E. Henry-Basch and P. Fréon (Lab. de Chim. P.C.B. IX, 11 rue Pierre-Curie, Paris). *Compt. Rend.*, 1959, **248** (18), 2597-2599.—The oxidation of penta-substituted glycerols with periodic acid has been studied. The glycerol, in aq. or aq. ethanolic soln. (0.0125 *M*, 45 ml), is treated with a mixture of 0.025 *M* periodic acid (60 ml), 20%  $\text{H}_2\text{SO}_4$  soln. (3 ml) and water (12 ml), and set aside at room temperature. The excess of periodic acid is then determined iodimetrically. Results are presented for 6 symmetrical and 3 asymmetric penta-substituted glycerols. These indicate that oxidation at first proceeds rapidly, with the consumption of one atom of O, and the rate then tends to a limit which represents complete oxidation with 2 atoms of O, and which is reached more rapidly with the asymmetric compounds (5 to 6 hr.) than with the symmetrical ones (25 to 35 hr.). It should be possible to arrest the reaction after the first stage by modification of the conditions. S. M. MARSH

**2766. Direct Karl Fischer determination of water in vinyl ethers.** L. Barnes, jun., and M. S. Pawlak (Air Reduction Co. Inc., Murray Hill, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1875-1876.—The direct determination of water in vinyl ethers by the Karl Fischer method is made possible by eliminating methanol from both the reagent and solvent. A stabilised reagent containing 2-methoxyethanol and a pyridine-glacial acetic acid solvent (5:2, by vol.) is suitable for the determination. Recoveries of water added to vinyl ethers were from 94 to 116%

at the 0.05% level, and 101% at the 1.26% level.

G. P. COOK

**2767. Spectrophotometric determination of aldoses by an iodimetric procedure.** G. L. Miller and A. L. Burton (Quartermaster Res. and Engrg Center, Natick, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1790-1793.—The sample soln. is treated with  $\text{Na}_2\text{CO}_3$  soln. and standard iodine - KI soln. After being set aside for a period of time at a temp. depending on the nature of the sugar being tested, the mixture is acidified with  $\text{H}_3\text{PO}_4$  and the excess of iodine is measured spectrophotometrically at 480 m $\mu$ . Glucose is used as the reference standard. Pentoses, hexoses, oligosaccharides and enzymic digests of carboxymethylcellulose were tested.

G. P. COOK

**2768. Detection and differentiation of sugars and polyols on single paper-chromatograms.** R. C. Bean and G. G. Porter (Dept. of Plant Biochem., Univ. of Calif., Riverside, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1929-1930.—Dip the chromatogram into a 1% soln. of *p*-anisidine hydrochloride (I) in butanol and heat at  $> 100^\circ$  or dip into a saturated soln. of benzidine hydrochloride (II) in ethanol and heat at  $> 120^\circ$  for 3 to 10 min. Mark the positions of the sugar spots. Then dip the paper into a freshly prepared mixture of saturated aq.  $\text{KIO}_4$  soln. and acetone (1:4) and allow to dry; the polyols appear as white or yellow spots on a purple (with I) or blue (with II) background. Both reactions may detect as little as 2.5  $\mu\text{g}$  of sugar or polyol on a normal one-dimensional chromatogram. Serine, some organic acids and high concn. of salt may yield spurious spots.

A. R. ROGERS

**2769. Periodate technique for the identification of sugar phosphates.** E. A. Davidson (Dept. Biochem., Duke Univ. Med. Center, Durham, N. Carolina, U.S.A.). *Nature*, 1959, **184** (Suppl. No. 18), 1395-1396.—Sugar phosphates are reduced with sodium borohydride to yield polyol phosphates. These are then oxidised with periodate. The sugar phosphate (1 to 10  $\mu\text{moles}$ ) is treated at pH 7.5 [tri(hydroxymethyl)methylamine buffer] with 2 molar equiv. of sodium borohydride. Reduction is allowed to proceed for 30 min. at room temp. and the pH is then adjusted to 4.5 with 6 *N* acetic acid. The excess of reducing agent is destroyed by heating for 3 min. in a boiling-water bath. A 20% molar excess of sodium periodate is then added and the periodate consumption is measured spectrophotometrically (cf. Morrison *et al.*, *J. Amer. Chem. Soc.*, 1955, **77**, 5156). The glycollaldehyde phosphate is adsorbed on a 1-ml Dowex 1-X8 (formate) column and eluted with 10 ml of 0.5 *N* HCl, and determined colorimetrically by the diphenylamine reaction (cf. Dische and Borenfreund, *J. Biol. Chem.*, 1949, **180**, 1297).

S. BAAR

**2770. Citric acid interference in the estimation of reducing sugars with alkaline copper reagents.** L. G. Paleg (Waite Agric. Res. Inst., Univ. of Adelaide, Australia). *Anal. Chem.*, 1959, **31** (11), 1902-1904.—In the analysis of reducing sugars by the molybdoarsenate modification of Somogyi's method (cf. *J. Biol. Chem.*, 1952, **195**, 19), citric acid will compete with tartaric acid in the alkaline copper reagent and greatly reduce the sensitivity of the reaction. A concn. of citrate as low as 0.00125 *M* shows the effect, which is greater in the assay of glucose than for fructose or maltose. The decrease in extinction is not directly proportional to the concn. of citric acid.

A. R. ROGERS

**2771. Separation and quantitative determination of methyl arabinosides using a starch column with an improved automatic control.** D. F. Mowery, jun. (New Bedford Inst. of Technol., New Bedford, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1911-1913.—The procedure and apparatus described previously (*cf. Anal. Abstr.*, 1958, **5**, 869) for the separation and determination of methyl mannosides has been modified for use with methyl arabinosides. A starch column replaces one of cellulose powder. A liquid pump is used to circulate the mixture of butanol, pyridine and water (10:3:3). An improved automatic control for the receiver enables fractions of equal vol. to be collected. A. R. ROGERS

**2772. Mass-spectrometric analysis. Re-arrangements in vinyl derivatives.** F. W. McLafferty (Eastern Res. Lab., The Dow Chemical Co., Framingham, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2072-2075.—The re-arrangement found in the mass spectra of polar unsaturated compounds can explain major anomalous peaks in vinyl ethers, vinyl esters and olefins. Such re-arrangement can be used to interpret the effects of substitution. K. A. PROCTOR

**2773. Paper chromatography of 2:4-dinitrophenylhydrazones of saturated aliphatic aldehydes.** V. R. Bhalarao and F. A. Kummerow (Dept. Food Technol., Univ. Illinois, Urbana, Ill.). *J. Amer. Oil Chem. Soc.*, 1959, **36** (10), 461-463.—The sharp separation of  $C_1$  to  $C_8$  aldehydes and some lower ketones, as their 2:4-dinitrophenylhydrazones, can be achieved in 3 hr. by an extension of the Silberstein method (*cf. Proc. Amer. Soc. Hort. Sci.*, 1954, **63**, 359). By using freshly prepared dry ethanediol-methanol (1:4) as stationary phase and developing with dry methanol-saturated *n*-heptane, reproducible results are obtained.  $R_F$  values for the derivatives of the  $C_7$ ,  $C_8$  and  $C_9$  aldehydes (0.89, 0.92 and 0.95, respectively) are unaffected by drying time, although the brown colour developed with 0.25 *N* ethanolic KOH fades rapidly. P. M. KINGSTON

**2774. Spectrophotometric titration of water in acetic acid.** S. Bruckenstein (Univ. Minn., Minneapolis, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1757-1760.—The sample, containing  $H_2SO_4$  as catalyst, is titrated with acetic anhydride and the absorption in the range 250 to 260  $m\mu$  is measured at each step of the titration. The extinction of the soln. changes only just before the end-point and then rises linearly with the concn. of excess of titrant. Extrapolation of the line to the blank extinction gives the end-point. The method was applied to concn. of 0.009 to 1.7% of  $H_2O$ . The precision and accuracy compared well with those of the Karl Fischer procedure. G. P. COOK

**2775. Use of tetraethylammonium hydroxide for the potentiometric titration of weak acids in non-aqueous solutions.** A. P. Kreshkov, L. N. Býkova and N. A. Mkhitarjan (D. I. Mendeleev Moscow Chem. and Technol. Inst.). *Zhur. Anal. Khim.*, 1959, **14** (5), 529-533.—A soln. of tetraethylammonium hydroxide (I) in benzene-methanol is used for the titration of strong, weak and very weak acids. A satisfactorily stable soln. is prepared by dissolving 30 g of air-dry tetraethylammonium iodide in 300 ml of abs. methanol,

shaking for 90 min. with 30 g of finely ground  $Ag_2O$ , filtering, and making the filtrate up to 1 litre with dry benzene; it is standardised against benzoic acid. The best solvent for the acids is ethyl methyl ketone. Pass a slow stream of *N* through 30 ml of ethyl methyl ketone and 2 or 3 drops of 0.3% methanolic thymol blue and titrate with I soln. to a blue colour; add 0.02 to 0.05 g of acid, stir magnetically and titrate with I soln. until the potential reaches a max. Acids which may be titrated include formic, acetic, propionic, adipic, anthranilic, oxalic, succinic, maleic, glutaric, tartaric, malic, camphoric, fumaric, benzoic, salicylic and phthalic, and their mixtures; weak acids such as the phenols and their mixtures with carboxylic acids; and HCl,  $HNO_3$ ,  $HClO_4$ ,  $H_2SO_4$ , and their mixtures with organic acids. Titration curves are given. C. D. KOPKIN

**2776. Determination of gluconic acid and citric acid. I. Determination of gluconic acid as a copper-gluconate complex.** H. Leopold and Z. Valtr (Julius Fučík Works, Kaznějov, Czechoslovakia). *Nahrung*, 1958, **2**, 464-475.—Gluconate (I) can be determined as the Cu-I complex by titration with thiosulphate after treatment of the soln. with KI and KSCN. For the determination of I in concn. of 1-8 to 6 mg per ml, add copper reagent (50 g of  $CuSO_4 \cdot 5H_2O$  per litre) (10 ml) to the phosphate buffer (33.1 g of  $Na_2HPO_4 \cdot 2H_2O$  per litre). After 15 min., add *N* NaOH (5 ml), followed by the soln. of I which has been made neutral to phenolphthalein. The vol. should not exceed 25 ml. After the addition of Supercel (0.3 g), filter the soln. and treat 30 ml of the filtrate with KI (5 g), dil. HCl (5 ml) and 20% KSCN soln. (5 to 7 ml). Titration to the starch end-point completes the analysis. In more dilute soln. of I (0.13 to 2.4 mg per ml), the procedure is identical, except that 2.5 ml of NaOH should be used instead of 5 ml. In spite of the coloured complex formed, the procedure is not suitable for colorimetric analysis. Substances that form copper complexes interfere, as do ions that form ppt. with the alkaline phosphate soln. or with  $SO_4^{2-}$  or copper ions.

**II. Determination of citric acid in the form of copper citrate.** H. Leopold and Z. Valtr. *Ibid.*, 1958, **2**, 532-546.—The method previously used for gluconic acid (*cf. Part I, above*) has been applied to citric acid.

**III. Analysis of important salts of gluconic and citric acids based on the formation of copper complexes.** H. Leopold and Z. Valtr. *Českosl. Farm.*, 1959, **8** (9), 486-489.—The method used in Part I has been applied to these salts. CHEM. ABSTR.

N. E.  
J. ZÝKA

**2777. Mass-spectrometric determination of hydroformylation products of ethyl sorbate.** R. E. Kourey, B. L. Tuffly and V. A. Yarborough (Union Carbide Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1760-1763.—Mass spectrometry can be used to determine the position of the formyl group in an analysis of the products from the hydroformylation of ethyl sorbate. The technique involves oxidation of the refined formyl esters, followed by esterification to form diethyl esters. The mass spectra of the diethyl esters are then used to calculate the amount of each component. Mixtures of known composition have been analysed with an average deviation of  $\pm 5$  to  $\pm 8\%$  from the known value. The pro-



cedure may also be applicable to the analysis of difficultly resolvable acids or aldehydes.

K. A. PROCTOR

**2778. Gas chromatography of the C<sub>1</sub> to C<sub>4</sub> nitro-paraffins.** R. M. Bethea and T. D. Wheelock (Chem. Engng Dept., Iowa State Univ. of Science and Technol., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1834-1836.—Eight nitroparaffins in the C<sub>1</sub> to C<sub>4</sub> series can be satisfactorily separated and determined with a precision of  $\pm 0.6\%$  and an accuracy within  $\pm 0.5\%$  under a variety of experimental conditions. Peak areas are used for calibration purposes.

K. A. PROCTOR

**2779. Properties of black chromium deposit and an analytical method for urea in the electrolytic bath.** Takeo Ishida, Yasuo Noda and Hideya Okada (Coll. of Engng, Univ. of Osaka Prefecture, Mozu, Sakai, Osaka). *J. Metal Finish. Soc. Japan*, 1959, **10** (10), 388-391.—For the determination of urea ( $> 0.05 M$ ) in a bath for black chromium plating (2.5 to 4 M CrO<sub>3</sub>, 0.05 M acetic acid and 0.05 M urea) the xanthhydrol method (Werner *et al.*, *J. Chem. Soc.*, 1920, **117**, 1356) is superior to the Hg(NO<sub>3</sub>)<sub>2</sub> method (Glassman, *Ber.*, 1906, **39**, 705) the error being  $< 2\%$ . The sample ( $\approx 10$  ml) is treated with a slight excess of BaCO<sub>3</sub> and filtered; the filtrate is mixed with xanthhydrol soln. (10%, 5 ml) and filtered after 1 hr., and the ppt. is washed with ethanol (10 ml) and dried at 100° for 30 min.

K. SAITO

**2780. Photometric determination of quaternary ammonium compounds with hexanitrodiphenylamine.** H. G. Schill (Royal Inst. of Pharm., Stockholm, Sweden). *Anal. Chim. Acta*, 1959, **21** (4), 341-352.—Quaternary ammonium ions are extracted from soln. of pH 11 with a soln. of hexanitrodiphenylamine (I) in CHCl<sub>3</sub> or dichloromethane. The base and I form a complex which passes into the organic layer and the excess of I passes into the aq. layer. Since different bases yield complexes with different mol. extinction coefficients, a large excess of tetrabutylammonium iodide is added to the extract and the extinction is measured at 420 m $\mu$ . Bases that contain several quaternary groups can only be extracted with dichloromethane from 3 N NaOH, and this provides a means of effecting certain separations.

H. N. S.

**2781. Determination of EDTA in the presence of condensed phosphates.** S. Schinzel (Anal. Lab., Chem. Fabrik Uetikon, Zürich). *Z. anal. Chem.*, 1959, **169** (6), 416-422 (in German).—Little or no interference occurs when EDTA is titrated at pH 4 with CuSO<sub>4</sub> with 1-(2-pyridylazo)-2-naphthol (I) as indicator, in the presence of a large excess of NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, Na<sub>6</sub>P<sub>3</sub>O<sub>10</sub> or Na<sub>x+2</sub>P<sub>3</sub>O<sub>3x+1</sub> provided that the vol. of titrant is small. *Procedure*—Dilute an aliquot ( $> 2$  g of phosphates) to 100 ml, add methyl orange and acidify with HCl (1:1) to pH 4. Boil, add 0.2 ml of a 0.1% ethanolic soln. of I and titrate with 0.1 M CuSO<sub>4</sub> to a wine-red end-point. If more than 5 ml is required, repeat with a smaller aliquot. For washing powders containing perborates and phosphates, dissolve 10 g in hot H<sub>2</sub>O and titrate as before, with an aliquot such that  $> 1$  ml of 0.1 M CuSO<sub>4</sub> is required; since this reaction is non-stoichiometric, multiply the vol. of titrant by a factor of 1.10. Calcium, Mg and small amounts of Fe do not interfere.

P. D. PARR-RICHARD

**2782. Polarographic determination of NN'-ethylenediglycine and nitrilotriacetic acid in (ethylenedinitrilo)tetra-acetic acid.** R. B. LeBlanc (Dow Chemical Co., Freeport, Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1840-1841.—The half-wave potentials of the Cd<sup>II</sup> chelates of NN'-ethylenediglycine (I) and nitrilotriacetic acid (II) are too close to give resolution of the two waves. The diffusion current of this double wave is used to measure the sum of these two components. I is then converted by hot acid soln. into a cyclic imide which does not form a stable chelate with Cd<sup>II</sup> under the conditions of the analysis. The II content of the sample can therefore be measured directly and the I content by difference. The accuracy of the method for each compound is generally within 10% and the limit of detection is about 0.01 millimole per litre.

G. P. COOK

**2783. Improved separation in gas chromatography by temperature programming. Application to mercaptans (thiols) and sulphides.** J. H. Sullivan, J. T. Walsh and C. Merritt, jun. (Quartermaster Res. and Engng Center, Natick, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1826-1828.—A method of non-linear programming with modified conventional equipment is described. The separation of a mixture of 12 thiols, boiling-range 35° to 220°, and of a mixture of 11 sulphides, boiling-range 37° to 235°, on a 7-ft. column of 25% of squalene on firebrick, programmed from 20° to 150°, is described.

K. A. PROCTOR

**2784. Evaluation of some simple sulphonic acids as non-aqueous titrants.** M. M. Caso and M. Cefola (Fordham Univ., New York, U.S.A.). *Anal. Chim. Acta*, 1959, **21** (4), 374-379.—Potassium hydrogen phthalate is titrated in acetic acid with 0.1 N soln. of methane-, ethane-, benzene- and naphthalene-sulphonic acids, the potentials being measured with a glass electrode and calomel reference electrode. The titration curves are reproduced. The max. dE/dV values are about two-fifths of that obtained when titrating with 0.1 N HClO<sub>4</sub>, but ppt. and gels are not formed when the sulphonic acids are used as titrants. The precision is 0.2 to 0.5%, and sharp colour-changes are obtained when crystal violet is used as indicator.

H. N. S.

**2785. Titrimetric determination of 2-mercaptoacetic (thioglycolic) acid by copper(II).** Suseela B. Sant and Bharat R. Sant (Mount Holyoke Coll., South Hadley, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1879-1880.—A standard soln. of CuSO<sub>4</sub> is titrated with thioglycolic acid, the end-point being indicated by the formation of a permanent yellow ppt. The reactions taking place during the titration are—the complexing of Cu with thioglycolic acid, reduction of Cu<sup>II</sup> to Cu<sup>I</sup> with simultaneous oxidation of thioglycolic to dithioglycolic acid and, at the end-point, the formation of yellow cuprous mercaptide. The accuracy is within 0.3%. Good agreement was attained with results by the iodimetric procedure.

G. P. COOK

**2786. Determination of xanthates and sodium diethyldithiocarbamate by extraction.** K. Bičovský and P. Bičová (Res. Inst. Metallurgy, Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 3099-3102 (in German).—The method is based on the extraction of Ni<sup>II</sup> xanthate with CHCl<sub>3</sub> and the titration of Ni<sup>2+</sup> with mercuric acetate soln. The method has been found to be suitable for the control



of the technical xanthates used in flotation procedures (even in  $10^{-4}$  M soln.), and can also be used for the determination of Na diethyldithiocarbamate. *Procedure*.—To the sample (containing 30 to 50 mg of xanthate) add a 1% soln. of  $\text{Ni}(\text{NO}_3)_2$  (25 ml) and shake for 1 min. with  $\text{CHCl}_3$  (10 ml). Transfer the  $\text{CHCl}_3$  layer into a 150-ml separating-funnel, and repeat the extraction with 10 ml of  $\text{CHCl}_3$ . Combine the  $\text{CHCl}_3$  layers and add buffer soln. (50 g of Na acetate and 50 ml of glacial acetic acid per litre) (15 ml) and titrate in the separating-funnel with 0.01 M mercuric acetate. After each addition of titrant the liquid must be thoroughly shaken. When the brown-yellow liquid becomes pale add a 1% soln. of diphenylcarbazone in  $\text{CHCl}_3$  (8 to 10 drops) and titrate to a red-violet end-point. The mean error is  $\pm 0.8\%$ . The method can be used in the presence of  $\text{SO}_3^{2-}$ ,  $\text{S}^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{CS}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , ethanol, hydroxides,  $\text{CS}_2$  and  $\text{CO}_3^{2-}$ . The method also yields good results if a lead salt and benzene are used instead of a nickel salt and  $\text{CHCl}_3$ .  
J. ŽYKA

2787. Application of the float method to the determination of traces of butanol in tributyl phosphate. W. Korpak and K. Majchrzak (Dept. of Chem. Technol. of Reactor Materials, Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1959, 4 (3), 571-576.—A method is described for the determination of butanol contents ranging from 0.05 to 0.5%. It is based on the azeotropic distillation of butanol with water, determination of the temperature of equilibrium of the distillate and a glass float, and evaluation of the results from a calibration curve. By multiplying the observed results by a factor of 1.12 an accuracy within  $\pm 2.3\%$  can be achieved.

W. B. MIASKOWSKI

2788. Indirect method of detection and determination of mono- and di-butyl phosphate in tributyl phosphate. S. Siekierski (Dept. of Radiochem., Inst. of Nuclear Res., Polish Acad. Sci., Warsaw). *Chem. Anal., Warsaw*, 1959, 4 (3), 551-556.—The method is based on the fact that Zr is not extracted from  $\text{N HClO}_4$  soln. by pure tributyl phosphate (I) unless it contains dibutyl phosphate (II) or monobutyl phosphate (III). A standard Zr soln. in  $\text{N HClO}_4$  is extracted with an equal vol. of I; the amount of Zr in the aq. phase is determined by complexometric titration and the I and III contents are read from a calibration curve. Although II and III cannot be determined separately the "total extractive capacity" can be found when both are present. The sensitivity for III is  $5 \times 10^{-5}$  ml per litre and for II is  $2 \times 10^{-5}$  ml per litre, and the error ranges from 2 to 5%, according to the concentration ( $3 \times 10^{-4}$  to  $1.5 \times 10^{-4}$  ml per litre). Butanol ( $> 5\%$ ) does not interfere.

W. B. MIASKOWSKI

2789. Separation of phosphoric acid esters by ion-exchange chromatography. H. Schmitz and G. Walpurg (Physiol.-chem. Inst., Univ. of Marburg/L., Germany). *Angew. Chem.*, 1959, 71 (17), 549-552.—Ion-exchange chromatography on Dowex 2-X10 at pH 6 to 6.5 permits the quant. separation of complex mixtures of nucleotides and other phosphate esters (10 to 20  $\mu$ moles of each component) derived from tissue extracts. Elution with dil. formic acid is practically quant., but recovery depends in part on the temp. since certain esters decompose at  $20^\circ$ . Phosphate determinations are supplemented by u.v. absorption spectrophotometry and paper chromatography.  
J. P. STERN

2790. Boron compounds. II. Gas-chromatographic analysis of trialkylboranes involving mass-spectrometric measurements. G. Schomburg, R. Köster and D. Henneberg (Max-Planck-Inst. f. Kohlenforsch., Mülheim-Ruhr). *Z. anal. Chem.*, 1959, 170 (1), 285-301.—Chromatographic separation followed by mass-spectrometric identification of the pure components affords a means of analysing mixtures of alkylboranes. The difficulty of removing traces of water and O from the apparatus and carrier gas, and a device for transferring the sample under a protective gas, are described. The conditions used and the results obtained with trialkylboranes are reported.  
G. BURGER

2791. Analysis of diphenyl-terphenyl organic coolant mixtures by gas chromatography. R. A. Baxter (Atomics International Div., N. American Aviation, Inc., Canoga Park, Calif.). *U.S. Atomic Energy Comm., Rep. NAA-SR-Memo-3793*, April, 1959. 8 pp.—Mixtures of diphenyl and terphenyls are being used as moderator-coolants. A gas-chromatographic method was developed for the quant. determination of diphenyl and ortho-, meta- and para-terphenyls in various coolant mixtures. The technique involves relating the peak heights of the components to the peak height of an added internal standard after determination of the appropriate calibration factors. The method was successfully used in the analysis of both unirradiated and irradiated coolant mixtures containing up to 4% of high-boiling constituents. The accuracy and precision of the method were checked by analysing four known synthetic mixtures. The average relative error obtained from 54 determinations was  $\pm 1.7\%$  with a range of  $+4.6$  to  $-6.4\%$ .  
NUCL. SCI. ABSTR.

2792. Determination of isopropylbenzene hydroperoxide by using "dead-stop" end-point indication. L. Tsuk and G. Zöllner (Res. Inst. for Ind. of Org. Chem. and Plastics, Budapest). *Magyar Kém. Lapja*, 1959, 14 (10), 417-418.—isoPropylbenzene hydroperoxide is determined iodimetrically by titrating the iodine liberated from KI with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  in glacial acetic acid. With coloured or non-transparent soln. the dead-stop method at 400 mV is recommended. The error is  $< \pm 0.8\%$ .  
G. SZABO

2793. Chromatography of phenolic substances with aqueous solutions of electrolytes. A. Resplandy (Lab. de Chim., Appl. aux Corps Org., Mus. Nat. d'Hist. Nat., Paris). *Ann. Pharm. Franç.*, 1959, 17 (6), 435-441.—The  $R_F$  values of 18 phenolic substances are determined by ascending chromatography over  $\approx 20$  cm on Whatman No. 1 paper, with water, acetic acid, HCl and aq.  $(\text{NH}_4)_2\text{SO}_4$  soln. of various concn. as solvents. The  $R_F$  of a particular compound varies rectilinearly with the concn. of acid or salt. The  $R_F$  values of homologues remain in the same order whatever the composition of the solvent. An increase in the number of hydroxyl groups of the phenol, or of the mol. wt., decreases the  $R_F$ . The presence of carboxyl groups lowers the  $R_F$  when aq. soln. of electrolytes are used, but increases it when water is used. Phenolic substances migrate less readily than their corresponding glycosides.  
E. J. H. BIRCH

2794. Separation of phenolic compounds on ion-exchange resins. G. Krampitz and W. Albersmeyer (Inst. für Anat. u. Physiol. der Haustiere, Univ. Bonn, Germany). *Experientia*, 1959, 15 (10), 375 (in German).—A new method is described for the

chromatographic separation of phenolic compounds (pH 3 to 3.4) on sulphonated polystyrene resin. Elution is carried out with a citrate buffer (pH 3.4).

P. NICHOLLS

**2795. Ultra-violet spectra of phenolic compounds.** N. I. Shergina, V. P. Kuznetsova, A. S. Nakhmanovich and I. V. Kalechits. *Acta Chim. Sinica*, 1959, **25** (5), 236-253.—Data are presented showing absorption bands and maxima of 31 phenolic compounds (0.01 to 0.06 g per litre in isooctane) between 2400 and 3500 Å. The introduction of radicals on phenolic compounds causes slight shifts of absorption maxima towards longer wavelengths, the extents depending on the types of radicals and the positions they take. The effect of substitution by hydroxyl groups is greater than that by alkyl groups, and the effect due to substitution at a position *para* to the hydroxyl group is greater than that at the *ortho* or *meta* positions. A method is described for the quantitative analysis of phenolic compounds in admixture, based on the fractional distillation of the sample and on the u.v. spectrum examination of individual components. The method has been successfully applied to 22 synthetic mixtures of phenolic compounds, with an error  $\pm 10\%$ .

S. H. YUEN

**2796. Gas-liquid chromatography: separation of close-boiling phenol isomers.** V. T. Brooks (Res. Dept., Midland Tar Distillers, Ltd., Four Ashes, nr. Wolverhampton, England). *Chem. & Ind.*, 1959, (42), 1317-1318.—The separation of phenol isomers with phosphate esters of various phenols as the stationary phase is discussed. The 2:4-xyleneol ester gives the best separation of *m*-cresol from *p*-cresol, and of 2:4-xyleneol from 2:6-xyleneol; a peak diagram shows results for a 10-component system. The packing consists of 5% w/w of stationary phase on acid-washed Celite.

P. D. PARR-RICHARD

**2797. Spectral detection of terminal-ring quinones.** E. Sawicki, T. W. Stanley and T. R. Hauser (R. A. Taft San. Engrg. Center Cincinnati, Ohio, U.S.A.). *Anal. Chim. Acta*, 1959, **21** (4), 392-395.—Various heterocyclic nitrogen compounds that are  $\text{CH}_2$ -substituted in a position *ortho* or *para* to N yield blue or green colours with quinones that contain the grouping  $\text{O}=\text{C}-\text{C}=\text{C}-\text{X}$ , where X is H or halogen. The reaction is carried out in 2-methoxyethanol as solvent, and tetraethylammonium hydroxide is added 10 min. after mixing the reactants. Sensitivities are given for the reactions of 9 quinones (including *p*-benzoquinone, 1:4-naphthaquinone and chloranil) with 5 substituted quinolines (including quinaldine and 1-ethyl-quinaldinium iodide), and the absorption maxima are quoted. A number of compounds that contain an activated methylene group, e.g., 3-ethylrhodanine, also yield sensitive colour reactions with the same class of quinones in alkaline dimethylformamide or 2-methoxyethanol.

H. N. S.

**2798. New volumetric methods for the analysis of organic substances. VI. Oxidation of mandelic acid with lead tetra-acetate and potassium periodate.** A. Berka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1959, **8** (10), 561-564.—Whereas only 40% of mandelic acid (I) is oxidised with potassium periodate to  $\text{CO}_2$  in alkaline, neutral or acid medium within 48 hr., a similar oxidation with lead tetra-acetate (II) soln. in anhyd. acetic acid is complete within 4 hr. and can be used for

volumetric purposes. For the determination of the excess of II, a method with quinol as reagent and ferroin as indicator is recommended. **Procedure**—Dissolve the sample (about 0.4 g of I) in anhyd. acetic acid and dilute with the same solvent to 50 ml. To an aliquot (5 ml) add 0.05 M II (10 ml), mix, and set aside for 4 hr. Add, with stirring,  $\text{H}_2\text{SO}_4$  (1:1) (6 ml) and ferroin soln. (2 drops) as indicator, and titrate with 0.05 N quinol till the soln. is orange. To avoid the indicator error titrate another portion of II (5 ml) with quinol, adding the indicator immediately before the end-point. Make a blank determination. The mean relative deviation is 0.42%. The volumetric soln. of II was prepared by dissolving  $\text{Pb}_3\text{O}_4$  at 55° in anhyd. acetic acid, crystallising and diluting the product in the same solvent. The factor was determined potentiometrically with hydrazine sulphate as volumetric reagent.

J. ZÝKA

**2799. Microchemical detection of phthalic acid.** H. Chomse and I. Arend (Inst. Veterinär-Chem., Humboldt-Univ., Berlin). *Chem. Tech., Berlin*, 1959, **11** (7), 377-379.—The conditions for max. sensitivity of this test, based on the formation of fluorescein, have been investigated. Phthalic acid ( $< 0.25 \mu\text{g}$ ) and resorcinol (1 mg) are heated for 15 min. at 80° with conc.  $\text{H}_2\text{SO}_4$  (0.01 ml). The cooled soln. is made alkaline with NaOH and exposed to the focused light from a special filament lamp, when the fluorescence is observed. A mercury arc should not be used, since it may excite a blue fluorescence difficult to distinguish from that of fluorescein. The reaction may be carried out at 130° for 5 min. provided that the molar ratio of  $\text{H}_2\text{SO}_4$  to resorcinol is raised to 40:1. Quantities of phthalic acid  $< 0.25 \mu\text{g}$  could not be detected with certainty.

A. R. PEARSON

**2800. Determination of organic nitro compounds by controlled-potential coulometry.** J. M. Kruse (E. I. du Pont de Nemours and Co., Gibbstown, N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1854-1857.—The cell design and coulometric apparatus were essentially those used by Lingane (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 150). Background effects, which were the main obstacle to the determination of nitro compounds, were partly eliminated by pre-electrolysis of the supporting electrolyte. Methanol-water systems were found to be the most satisfactory solvents and a methanol-water soln. (4:1), 0.1 M in LiCl, was used for most nitro compounds. At optimum sample concn. (requiring 100 to 150 coulombs) the standard deviation was  $\pm 1\%$ , and as little as 20 p.p.m. of a nitro compound could be measured.

G. P. COOK

**2801. Detection of primary aromatic amines.** Ya. D. Mogilyanskii. U.S.S.R. Pat. 119,375 (April 15, 1959).—Primary aromatic amines are detected by means of a soln. of  $\text{CuCl}$  (I) in pyridine in the presence of  $\text{CCl}_4$ . Place 1 drop of a 10% I soln. in conc. HCl on a filter-paper, add 2 drops of pyridine and 1 drop of  $\text{CCl}_4$ , and then 1 or 2 drops of the test soln. Within 10 to 30 sec. (or up to 2 or 3 min. for very dil. soln.) a characteristic colour is formed. Clear and rapid colour reactions are obtained at the following dilutions—aniline 1 in  $10^4$ , 2-naphthylamine 1 in  $2 \times 10^4$ , and benzidine 1 in  $10^4$ ; a less clear and slower reaction is given by aniline at 1 in  $2 \times 10^4$  and by 2-naphthylamine at 1 in  $3 \times 10^4$ . The colour obtained is red-orange for aniline, and *p*- and *m*-nitroanilines; orange-red for *p*-toluidine, 2:4-xylidine, 1-naphthylamine and *m*-chloroaniline;

red for *p*-anisidine, *o*-anisidine, *o*-aminophenol, 2-naphthylamine and sulphonic acid; crimson for *p*-aminophenol and *o*-toluidine; and violet for benzidine. No colour is given by phenols (phenol, 2-naphthol, phloroglucinol), aliphatic amino acids (leucine, glutamic acid, methionine), acetamide, acetoxime, urea, thiourea or acetanilide. Free *N*-ethyl- and dimethyl-aniline or conc. soln. of their hydrochlorides give a yellow colour; however, the addition of HCl (1:3) gives a clear yellow soln., while primary aromatic amines give a ppt., usually bright red.

C. D. KOPKIN

**2802. Determination of aromatic amines by column chromatography of azo derivatives.** L. Nebbia and B. Pagani (Ist. "G. Donegani," Soc. Montecatini, Novara). *Chim. e Ind.*, 1959, **41** (9), 872-874.—Aromatic amines are separated by chromatography on a mixture of magnesium oxide and 10 to 15% of magnesium hydroxide after being converted into their azo derivatives with diazotised *p*-nitroaniline. By this method it is possible to separate 5 to 10- $\mu$ g amounts of a mixture of aniline and *o*-, *m*- and *p*-toluidines; *o*-, *m*- and *p*-anisidines; aniline and diphenylamine; and 1- and 2-naphthylamines. Suitable eluents are tabulated.

C. A. FINCH

**2803. Determination of diphenylamine as a stabiliser in trichloroethylene.** J. Hryniewicz and Z. Grapich (Inst. of Chem. Synthesis, Oświęcim). *Chem. Anal., Warsaw*, 1959, **4** (3), 619-620.—To a sample (150 ml  $\approx$  217.9 g) of trichloroethylene (I) stabilised with diphenylamine (II) is added 150 ml of an 80% soln. of acetic acid, the mixture is cooled to 15° and titrated with 0.1 N NaNO<sub>2</sub> until a drop of the mixture placed on a wet starch-iodide paper turns it blue; the end-point is reached when, after 5 min. from the addition of the last drop of titrant, the test paper still turns blue. A blank titration is carried out with 150 ml of I free from II. The method gives results higher than the theoretical by 0.001 to 0.002%, but is sufficiently accurate for routine work, and requires  $\approx$  15 min. Phenol and 1-naphthol present in quantities smaller than that of diphenylamine do not interfere.

W. B. MIASKOWSKI

**2804. Determination of isomeric distribution in mixed toluene-*o*- and -*p*-sulphonamides by ultraviolet absorption.** F. N. Stewart, J. E. Caldwell and A. F. Uelner (Monsanto Chemical Co., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1806-1808.—The toluene-*o*- and -*p*-sulphonamide contents are determined by differential measurement at 256 and 276 m $\mu$ . Interferences are removed by prior extraction with CHCl<sub>3</sub> from an alkaline soln. of the sample. The standard deviations are within  $\pm$  1% absolute.

G. P. COOK

**2805. Determination of *p*-phenylenedilithium by potentiometric titration with cerium(IV) nitrate solution.** A. F. Clifford and R. R. Olsen (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1860-1861.—The method is based on the oxidation and hydrolysis of *p*-phenylenedilithium to form quinol, which is measured by potentiometric titration with standard Ce(NO<sub>3</sub>)<sub>3</sub> soln. The method is selective for *o*- or *p*-phenylenedilithium in the presence of other types of monometallo organic compounds.

G. P. COOK

**2806. Separation and identification of six arseno-organic compounds by paper chromatography: arsanilic acid, arsenosobenzene, arspenamine,**

**4-hydroxy-3-nitrophenylarsonic acid, 4-nitrophenylarsonic acid and *p*-ureidophenylarsonic acid.** L. C. Mitchell (Division of Food, Food and Drug Administration, Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (4), 684-692.—The six compounds are separated by two-dimensional chromatography on sheets (8 in.  $\times$  8 in.) of Whatman No. 1 paper, with solvents (a) water (20 ml) and HNO<sub>3</sub> (2 ml) diluted to 100 ml with methyl cyanide, and (b) water (30 ml) and aq. NH<sub>3</sub> (5 ml) diluted to 100 ml with methyl cyanide. The compounds are located in the chromatogram and identified by their quenched or fluorescent areas in u.v. light. The areas visible in u.v. light may be reproduced for inspection in daylight by printing on to blueprint paper by means of exposure to a germicidal lamp. Final identification is made by spraying with (i) ethanolic ammoniacal silver nitrate and (ii) ethanolic pyro-gallol, with air-drying between the sprayings. Identification limits are 1  $\mu$ g for each compound.

E. C. APLING

**2807. Preparation and infra-red spectra of the three ethylcyclopentenes, methylene- and ethylenecyclopentane.** S. Pinchas, J. Shabtai, J. Herling and E. Gil-Av (Weizmann Inst. Sci., Rehovoth, Israel). *J. Inst. Petrol.*, 1959, **45**, 311-315.—Infra-red spectra of 1-, 3- and 4-ethylcyclopentene, ethylenecyclopentane and methylenecyclopentane are reproduced.

**2808. Determination of pentosans. III. Bromatometric determination of furaldehyde.** P. O. Bethge (Swedish Forest Products Res. Lab., Stockholm). *Svensk Papp-Tidn.*, 1958, **61** (9), 267-271 (in English).—A study of the factors affecting the furaldehyde (I) - bromine reaction (applied to Tollens distillates) reveals that the experimental conditions must be carefully chosen in order to achieve the quant. reaction of one mole of I with two equiv. of Br. *Procedure*—Take an aliquot (50 ml) of the distillate (*Ibid.*, 1941, **44**, 267), add 6.5  $\pm$  0.1 M NaOH (25 ml) and cool to 15° to 30°. Add 4 M KBr (5 ml) and 0.025 N KBrO<sub>3</sub> (20 ml). Set aside for exactly 2 min., add M KI (10 ml), mix and add 4 M Na acetate (10 ml). Titrate immediately with 0.01 N Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> with starch as indicator. Best results are obtained if vacuum flasks (*Anal. Abstr.*, 1954, **1**, 72) are used. Results obtained on "synthetic" Tollens distillates show recoveries of 99.4 to 100.2%. 5-Hydroxymethylfuraldehyde (II) is quant. titrated by the given procedure. Formaldehyde does not interfere.

**IV. Bromatometric method for the determination of furaldehyde and 5-hydroxymethylfuraldehyde in Tollens distillates.** P. O. Bethge. *Ibid.*, 1958, **61** (18), 565-567, 856.—The method is based on the differences in the distribution of I and II between aq. HCl soln. and CHCl<sub>3</sub> (*cf. Anal. Abstr.*, 1958, **5**, 126). The distribution coeff. at 25° for I and II are 16.51  $\pm$  0.10 and 0.254, respectively (3.82 M HCl in the aq. phase). *Procedure*—Determine the total I and II in an aliquot of the distillate by the method given above. To another aliquot (100 ml) add CHCl<sub>3</sub> (25 ml) that has previously been shaken with water. Shake for 1 min. and set aside at 25° for 10 min. Shake again for 1 min., separate the phases and use a portion (50 ml) of the aq. phase for a second titration. Formulae are given for the calculation of the concn. of I and II from the two results. Test experiments show recoveries of 96.0 to 100.6% for I and 101 to 114% for II. Results for distillates from different celluloses are given.

B. RÖNNHOLM



2809. The use of gas chromatography for analytical control of the production of crude naphthalene oil and its processing into pure naphthalene. M. Hřivnáč and J. Janák (Lab. Analysis Gases, Acad. Sci., Brno, Czechoslovakia). *Chem. Průmysl*, 1959, 9 (9), 459-464.—By the procedure described, 15 fractions were found in crude naphthalene oil and intermediates, and their chromatographic spectra were determined. The value of gas chromatography for process control is stressed. J. ŽYKA

2810. Chromatography of dye intermediates. X. Chromatographic separation of hydroxy and amino derivatives of naphthalene. J. Latínka (Východočeské Chem. Závody, Synthesia, Pardubice-Semtin, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, 24 (9), 2939-2947 (in German).—The chromatographic separation of 1- and 2-naphthol, dihydroxynaphthalenes, 1- and 2-naphthylamine, N-phenyl-1- and -2-naphthylamine and of several diamionaphthalenes and aminonaphthols has been achieved. The separation was carried out on Whatman No. 4 paper (impregnated with a 10 to 30% methanolic soln. of formamide or dimethylformamide) with an ethanolic soln. of  $\approx 20 \mu\text{g}$  of the substance. The following combinations of solvents were used—formamide or benzene-ethyl acetate (4:1); formamide or  $\text{CHCl}_3$ -ethyl acetate (4:1); formamide- $\text{CHCl}_3$ ; formamide- $\text{CCl}_4$ ; formamide-cyclohexane; dimethylformamide-cyclohexane. The separated spots can be detected by fluorescence in u.v. light or with diazotised *p*-nitroaniline, or with a mixture of  $\text{FeCl}_3$  and  $\text{K}_3\text{Fe}(\text{CN})_6$ . The sensitivity of the detection in u.v. light can be increased by exposing the chromatogram to fumes of  $\text{NH}_3$ ;  $0.2 \mu\text{g}$  of the substance can be thus detected. The method was used for the analysis of technical products of 1- and 2-naphthol, naphthylamine and N-phenylnaphthylamine. The selection of a suitable solvent and of a suitable stationary phase for weakly polar and difficultly sol. compounds is discussed. J. ŽYKA

2811. Nitration of naphthalenesulphonic acids. I. Polarography of mononitro derivatives of naphthalene-1:5- and -1:6-disulphonic acids. J. Horyna and V. Jehlička (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, 24 (10), 3353-3361 (in German).—In reaction mixtures obtained by the mono-nitration of soln. of naphthalene-1:5- or -1:6-disulphonic acids in  $\text{H}_2\text{SO}_4$  the  $\alpha$ -nitro isomers can be determined polarographically in the presence of  $\beta$ -derivatives. A linear relation between half-wave potentials of nitronaphthalenedisulphonic acids and the function  $H_0$  (Hammett, "Physical Organic Chemistry," 1st Ed., N.Y., 1940, p. 267) was found in  $\text{H}_2\text{SO}_4$  medium. The dependence of half-wave potentials and of limiting currents on pH ( $> 7$ ) can be explained by the production of aci-forms. *Procedure*—Treat the reaction mixture (containing  $\approx 0.0007$  mole of the nitro component in 36.05 g of conc.  $\text{H}_2\text{SO}_4$ ) with 50 g of ice, transfer it to a 500-ml flask and dilute with  $\text{H}_2\text{O}$  to vol. To 25 ml add 2.5 N  $\text{H}_2\text{SO}_4$  (20 ml) and a 0.5% soln. of gelatin in 0.1 N  $\text{H}_2\text{SO}_4$  (0.2 ml); dilute to 50 ml with  $\text{H}_2\text{O}$ , mix and register the polarographic wave. J. ŽYKA

2812. Gravimetric determination of anthraquinonesulphonic acids with benzidine. M. Matrká, F. Navrátil and B. Smetana (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1959, 9 (8), 415-416.—The formation of insoluble salts of anthraquinonesulphonic acids (I) with

benzidine was used for the rapid determination of I in control testing, with an error of  $\pm 1.2\%$ . *Procedure*—Dissolve the sample (0.2 g) in  $\text{H}_2\text{O}$  (60 ml) and 2.5 N HCl (20 ml) by heating. Then add a hot soln. of benzidine (1 g of benzidine in 10 ml of conc. HCl and 80 ml of  $\text{H}_2\text{O}$ ) (20 ml). Set aside for 1 hr. in an ice bath and filter through a G3 filter. Wash the residue with cold  $\text{H}_2\text{O}$  ( $3 \times 5$  ml) and dry at  $105^\circ$ . One mole of the monosulphonic acid reacts with 0.5 mole of benzidine, whereas disulphonic acids react with the reagent in the ratio 1:1.

J. ŽYKA

2813. Amperometric titration of anthraquinone-sulphonic acids with benzidine solution. M. Matrká and Z. Ságner (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Coll. Czech. Chem. Commun.*, 1959, 24 (10), 3249-3252 (in Russian).—The method is based on the formation of a difficultly sol. salt with benzidine. The amperometric titration is possible owing to the polarographically active behaviour of anthraquinone compounds on the dropping mercury electrode. The determination is not influenced by the presence of alkali sulphates. *Procedure*—Dissolve the sample (1.55 g) (1 g in the case of disulphonic acids) in  $\text{H}_2\text{O}$  and dilute to 1 litre. Transfer an aliquot (50 ml) to a titration vessel, add 2.5 N HCl (5 ml) and remove O by bubbling with N for 10 min. Titrate amperometrically with a 0.025 M benzidine soln. at  $-0.5$  V (Na anthraquinone-1-sulphonate),  $-0.7$  V (Na anthraquinone-2-sulphonate),  $-0.9$  V (K anthraquinone-1:5-disulphonate),  $-0.6$  V (Na anthraquinone-1:8-disulphonate), Na anthraquinone-2:6-disulphonate), or  $-0.4$  V (Na anthraquinone-2:7-disulphonate). J. ŽYKA

2814. An example of isomerisation in gas chromatography. M. Vilkas and N. A. Abraham (Lab. de Chim., École Norm. Sup., 24 rue de Lhomond, Paris). *Bull. Soc. Chim. France*, 1959, (10), 1651-1652.—Gas-phase chromatography of  $\beta$ -pinene, with N as carrier gas, on silicone (Elastomer E 301) supported on crushed brick at  $125^\circ$ , gives two sharply defined peaks, instead of the usual flattened peak characteristic of isomerisation, showing that isomerisation takes place rapidly at the start of the column, the components so formed being separated on the rest of the column. The first peak is shown by its i.r. spectrum to be a mixture of  $\alpha$ -pinene and camphene, and the second to be limonene. Similar isomerisation is observed with a freshly prepared column of silicone supported on Celite but, after 100 hr. of use, isomerisation no longer takes place. Columns impregnated with polyoxyethylene glycol (Polyglycol 400) or with "Ucon 50 HB" do not cause isomerisation, and only a single peak of  $\beta$ -pinene is obtained. That the isomerisation is due to the support was shown by pyrolysing 20 ml of  $\beta$ -pinene at  $125^\circ$  in a stream of N on 40 g of crushed refractory brick. The products recovered (16 ml) consisted of  $\alpha$ -pinene (30%), camphene (40%), limonene (15%), unchanged  $\beta$ -pinene (5%) and unidentified substances (10%).

E. J. H. BIRCH

2815. Quantitative determination of piperazine in the presence of ethylenediamine and diethylenetriamine. L. Nebbia and B. Pagani (Ist. "G. Donegani", Soc. Montecatini, Novara). *Chim. e Ind.*, 1959, 41 (9), 870-872.—The quant. determination of piperazine in the presence of ethylenediamine is carried out by precipitating with  $\text{CuSO}_4$  soln.; ethylenediamine is determined colorimetrically as the copper complex in solution. In the presence



of diethylenetriamine, piperazine cannot be determined as a ppt.; potentiometric titration or a two-indicator titration can be used; diethylenetriamine is determined as a copper complex. For small amounts of piperazine in ethylenediamine, the reaction between the NH group and acetaldehyde with sodium nitroprusside is applied; the  $\text{—NH}$  groups of diethylenetriamine interfere with the reaction.

C. A. FINCH

**2816. Determination of the water content of pyridine bases by dielectric measurements and by the use of molecular sieves for differential drying.** F. Oehme (Inst. zur Entw. Chem.-phys. Analysenmethoden, Weilheim/Obb.). *Angew. Chem.*, 1959, **71** (18), 572-574.—The linearity of the relationship between the dielectric constant and the water content ( $> 5\%$ ) of the pyridine bases is demonstrated. A dielectric-constant determination before and after drying with a molecular sieve gives the slope of the line and establishes the composition of a particular binary mixture so that the water content may be read off directly.

E. G. CUMMINS

**2817. Determination of isonicotino- and nicotino-nitriles in mixtures obtained after oxidation of picoline bases with ammonia.** W. Czerwinski (Gen. Chem. Inst., Warsaw). *Chem. Anal., Warsaw*, 1958, **3** (1), 53-63.—(a) Distil the mixture containing not more than 0.1 g of isonicotinonitrile (I) and nicotinonitrile (II) over MgO into standard HCl. (b) Treat the residue with NaOH and re-distil into another receiver containing standard HCl. (c) Take the same amount of soln. as in (a), add NaOH and distil immediately into standard HCl. Then the content of nitriles =  $c - (a + b)$ . For the determination of nitriles in the presence of high concn. of  $\text{NH}_3$ , (d) heat the sample containing I + II with 0.2 N NaOH in fivefold excess. Distil off all the bases and  $\text{NH}_3$  with steam. Dissolve the residue in 0.2 N HCl and remove  $\text{CO}_2$ . Titrate the excess of HCl. (e) From a known vol. of soln. distil off I + II with steam and treat the residue as in (d). The difference  $d - e$  gives the equivalent of total nitriles.

L. SMAKOWSKI

**2818. Ultra-violet spectrophotometric determination of quinoline and isoquinoline. I. Choice of solvent, and their simultaneous determination.** Motohisa Furusawa, Tsugio Takeuchi and Kazuhiko Kamijo (Fac. of Engng. Yamanashi Univ., Motoyanagi-cho, Kofu). *Coal Tar. J. Japan. Tar Ind. Ass.*, 1959, **11** (5), 238-241.—The absorption spectra of quinoline (I) and isoquinoline (II) were examined in various solvents and it was found that 0.05 M NaOH is most suitable for their simultaneous determination. Their individual extinction coeff. are proportional to the concn. ( $< 25 \mu\text{g}$  per ml) at 312.7 (max. for I), 319 (max. for II) and 207  $\mu\text{m}$ , where the difference is greatest; they are not affected by  $\text{Na}_2\text{SO}_4$  ( $< 0.05 M$ ) and  $\text{Na}_2\text{CO}_3$  (0.01 M). The amounts are calculated from these three values by the use of empirical equations. The sample (fractionated quinoline) is dissolved in 0.05 M  $\text{H}_2\text{SO}_4$  and diluted to 100 ml, and an aliquot (to give 10 to 25  $\mu\text{g}$  per ml in the final soln.) is made up to 50 ml with 0.05 M NaOH for spectrophotometry.

K. SAITO

**2819. Note on the u.v. spectra of compounds containing C=S groups.** R. Zahradnik (Inst. Hyg. and Ind. Diseases, Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 3193-3194 (in German).—During the systematic study of the spectra of compounds containing  $\text{X—}\overset{\text{O}}{\underset{\text{O}}{\text{C}}}=\text{S}$  groups ( $\text{X} = \text{C, N, O}$

or S) the spectrum of 2:5-dimercapto-1:3:4-thiadiazole was examined. Instead of the expected max. in the range 275 to 300  $\mu\text{m}$ , which is characteristic for compounds of this type, a max. at 332  $\mu\text{m}$  was found. The max. of 2-mercaptobenzothiazole occurs in the same region.

J. ZÝKA

**2820. Determination of trace amounts of water in hydrocarbons.** A. F. Pyrah and R. S. Robertson (Mobil Oil Co., Coryton, Essex, England). *J. Inst. Petrol.*, 1959, **45**, 316-319.—A modification of the Karl Fischer titration is described. A small potential is applied across two platinum electrodes immersed in a methanolic solution, when, on addition of a slight excess of reagent, the electrodes are depolarised and the p.d. falls. By employing a high-resistance millivoltmeter, water contents up to 100 p.p.m. can be determined with a precision of 2 to 4 p.p.m. A conical flask with two side-arms is used and precautions are taken to exclude moisture, the reagent being introduced by means of a micro-syringe.

D. DE VOY

**2821. Estimation of trace water content in a halogenated oil by means of tritiated water.** J. F. Cameron, I. S. Boyce and R. M. Glaister (Isotope Div., A.E.R.E., Harwell, Berks.). *Brit. J. Appl. Phys.*, 1959, **10** (10), 463-465.—By the use of the simple method described, involving tritiated water with an activity of 50 mC per ml, the water content of a fully halogenated hydrocarbon oil (Fluorolube) may be determined in concn. as low as 0.04 p.p.m. The labelled water content is not changed appreciably by exposure to the atmosphere.

E. G. CUMMINS

**2822. Studies in bomb calorimetry. X. Conditions for the combustion of solid and liquid fuels.** R. A. Mott and C. Parker (British Coke Res. Ass. Res. Centre, Chesterfield, Derbyshire, England). *Fuel, London*, 1959, **38** (2), 189-204.—The examination of the gases remaining in a calorimeter after combustion indicated that fuels such as coke, anthracite, benzene and gas oil, which tend to leave a carbonaceous residue, often produce significant quantities of CO, even when no residual carbon can be detected. By means of a bomb fitted with observation windows, the flame period and total combustion period for a number of fuels and benzoic acid were measured, and, by a correct choice of crucible dimensions and oxygen pressure, it proved possible to make these combustion characteristics approximately the same for all fuels and at the same time to ensure that the residual gases contained  $< 30$  p.p.m. of CO. Procedures are recommended for the combustion of benzoic acid, coal, anthracite, coke, benzene, gas oil, aviation spirit and isopentane which allow a constant length of chief period (Barker *et al.*, *Ibid.*, 1955, **34**, 283) to be employed for any given calorimeter. For fuels other than coke the time giving the best reproducibility in determinations of effective heat capacity should be used, while for coke a somewhat longer time is necessary.

W. T. CARTER

**2823. Flame-photometric determination of lead and manganese in gasoline.** G. W. Smith and A. K. Palmby (Res. Lab., Ethyl Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1798-1802.—In each method the sample is burned in an oxy-hydrogen flame. The effects of differences in base-stock composition are eliminated in the lead method by using an incremental addition of lead for calibration, and minimised in the manganese method by

diluting the sample at least twenty-fold with iso-octane. The precision for Pb (as tetraethyl-lead) is  $\pm 2\%$  and the concn. range 0.1 to 6 ml per gallon. The precision for Mn [as (methylcyclopentadienyl)manganese tricarbonyl] is  $\pm 3\%$  and the concn. range 0.1 to 4.0 g per gallon.

G. P. COOK

**2824. Determination of tetraethyl-lead in gasoline by titration with (ethylenedinitrilo)tetra-acetate.** M. Brandt and R. H. Vanden Berg (Ethyl Corp., Detroit, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1921.—The tetraethyl-lead is extracted from the sample by using the hot HCl extraction procedure of the ASTM chromatate and polarographic methods. The tetraethyl-lead is then decomposed, the lead salt is dissolved in water and subsequently determined by titration with EDTA (disodium salt), with copper-1-(2-pyridylazo)-2-naphthol as indicator. The results agreed well with those obtained by the ASTM method and the spread between replicates was generally 0.02 ml of tetraethyl-lead per gallon. Recoveries were  $> 98\%$ .

G. P. COOK

**2825. Formolite reaction. [Determination of aromatic hydrocarbons in mineral oils.]** M. Krajčević, B. Prohaska, D. Herman and D. Engel (Dept. of Org. Chem. Technol., Zagreb Univ.). *Kem. u Ind., Zagreb*, 1959, **8** (9), 231-235.—The quantitative method described is based on the formolite reaction (cf. Nastukov and Davidov, *Petroleum Z.*, 1930, **26**, 78). A 0.5-g sample is diluted in liquid paraffin in a 1:20 ratio and a 20-fold amount of  $H_2SO_4$  is added. After shaking the mixture for 20 min. at a constant temp. of  $20^\circ \pm 0.1^\circ$ , 0.1 ml of 36% formaldehyde soln. is added and the mixture is shaken for a further 15 min. The acid layer is separated after 1 hr., the extinction is measured, and the aromatic hydrocarbon content of the sample is read directly from calibration curves prepared for each type of mineral oil. Results were accurate to within 0.5% and the method was suitable for the industrial control of the removal of aromatic hydrocarbons from lubricating oils by extraction, hydrogenation or absorption.

A. L. GROCHOWSKI

**2826. Determination and behaviour of porphyrin aggregates in petroleum residues and bitumens.** G. Costantinides, G. Arich and C. Lomi (Univ. Trieste, Italy). *Chim. e Ind.*, 1959, **41** (9), 861-870.—The Groennings modification of the Treibs method for the determination of porphyrin contents in petroleum residues (cf. *Anal. Chem.*, 1953, **25**, 938) is revised to give a repeatability within 3%. A detailed analytical procedure is given for the porphyrins and for the Ni and V (not all of which is extracted with the porphyrins), based on spectrophotometric measurements, with suitable calibration curves. The effect of variations in procedure, including conditions of extraction, and solvents, is studied.

C. A. FINCH

**2827. Spectrographic determination of vanadium and iron in petroleum coke.** M. S. Vigler and A. L. Conrad [Standard Oil Co. (Ohio), Cleveland 28, Ohio, U.S.A.]. *Appl. Spectroscopy*, 1959, **13** (5), 122-123.—Coke free from volatiles is powdered and dried and excited in a 2-amp. spark-ignited a.c. arc. The samples are mixed in equal proportions with an internal standard - buffer mixture of 1 g of  $GeO_2$  with 0.010 g of  $InO_3$  and 0.008 g of  $PtO_2$ . Over the range 0.001 to 0.05% of V and Fe, the results agreed within  $\pm 10\%$  with those obtained by a longer colorimetric procedure.

P. T. BEALE

**2828. Calcium-base greases.** British Standards Institution (2 Park St., London, W.1). B.S. 3223: 1960, 29 pp.—Requirements are specified for lubricating greases comprising lubricating oils of petroleum origin and calcium soaps of fatty acids.

N. E.

**2829. Determination of solvent impurities in waxes and lubricating oil stocks by gas-liquid chromatography.** L. R. Durrett (Houston Refinery Lab., Shell Oil Co., Tex., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1824-1825.—The technique described offers a reproducible, accurate and relatively rapid procedure for determining 0.001 to 0.05% of ethyl methyl ketone and toluene. The sample is weighed, heated, and stripped with the carrier gas (He) until all the solvents have been removed and retained in a trap at  $-50^\circ$ . The trap is heated to flash the solvent impurities into a 10-ft. column of 30% of Carbowax "22" on firebrick at  $100^\circ$ . The method could be applied to the determination of other volatile impurities.

K. A. PROCTOR

**2830. The sampling of coal and coke. Part 1. Sampling of coal.** British Standards Institution (2 Park St., London, W.1). B.S. 1017: Part 1: 1960, 29 pp.—Requirements are specified for lubricating greases comprising lubricating oils of petroleum origin and calcium soaps of fatty acids.

N. E.

**2831. Methods for the analysis and testing of coal and coke. Part 9. Phosphorus in coal and coke.** British Standards Institution (2 Park St., London, W.1). B.S. 1016: Part 9: 1960, 16 pp.—A volumetric and a colorimetric method are specified.

N. E.

**2832. Determination of moisture in brown coal and its low-temperature coke by high-frequency heating.** J. Jandásek (Stalinwerken Nationalunternehmen, Žaluzi v Krušných Horách, Czechoslovakia). *Brennst.Chemie*, 1959, **40** (10), 309-314.—Brown coal is a polar non-conducting substance which, when dry, has a dielectric constant of  $\approx 5$ ; this rises with moisture content. With inductive heating, the temp. falls from the inside outwards, and the rate of heat generation decreases as  $H_2O$  is expelled, so that overheating and oxidation are avoided. The sample (10 g) is distributed evenly on a 12-cm filter-paper which is laid on a layer ( $\approx 3$  mm thick) of felt resting on the lower electrode of a generator such as is used for heating plastics, of output  $\approx 1.5$  kW at frequency  $17 \times 10^6$  ( $\pm 15\%$ ) c/s at a voltage adjustable at 3000 to 7000 V. After heating for 12 min. the sample is removed, wrapped in the filter-paper, cooled in the desiccator and weighed. The results agree within practical limits with those by distillation in xylene, with a slightly better precision.

A. R. PEARSON

**2833. The determination of volatile matter [in coal and coke] by the nitrogen tube method. II. Influence of the initial temperature.** Jiro Nitadori, Yutaka Koenuma and Kiyoshi Koseki (Resources Res. Inst., Kawaguchi, Saitama-ken). *J. Fuel Soc. Japan*, 1959, **38** (8), 536-541.—The determination of volatile matter by the B.S. 1016: 1942 method was examined with reference to the initial heating temp. The results for anthracite and coke were not affected by the initial temp. and agreed with those by the crucible method. For non-caking or weakly caking coal, the figures increased with rise of initial temp. and there was a significant difference between the results obtained by the specified nitrogen tube

method and those by the rapid heating method, the latter being in better agreement with those by the crucible method. The nitrogen tube method can be calibrated by means of an empirical diagram.

K. SAITO

**2834. Gas chromatography at high temperature. Application to coal tar and its derivatives.** F. Dupire (Soc. Carbochim. S.A. Tertre, Belgium). *Z. anal. Chem.*, 1959, **170** (1), 317-326.—A chromatograph for use up to 400° is described. The column and thermal-conductivity cell are made in one piece from Pyrex glass. The stationary phase is silicone grease on fire-brick. At 360° a 6-metre column has the equivalent of 3500 theoretical plates. Reoplex 400 polyester can be used as a polar phase up to 275°. By a combination of chromatography and i.r. spectrometry, several coal products have been quantitatively analysed.

G. BURGER

**2835. Gas-chromatographic analysis of coal products, especially those with high-boiling fractions.** H. Ritter and H. Schnier (Rheinische Bergbau A.-G., Gelsenkirchen). *Z. anal. Chem.*, 1959, **170** (1), 310-317.—A suitable stationary phase for use up to 185° is polyoxyethylene glycol of mol. wt. 20,000 supported on Sterchamol; He is the carrier. A short, expendable pre-column is described for use with samples of tar or tar oil which foul the column. A study of the composition of the products in relation to the coke-oven conditions is reported. Of particular importance is the determination of aliphatics, of naphthalene and of the toluene ratio. Retention times of 24 products relative to benzene are listed.

G. BURGER

**2836. Conventional and derivative polarography for the analysis of coal-tar products.** A. G. Pozdeeva, N. Kh. Cherkasov and F. L. Kruglova. *Zhur. Prikl. Khim.*, 1959, **32** (9), 1973-1978.—A study has been made of the determination of pyridine and its homologues and pyridine bases by means of conventional and derivative polarography. A proportional relationship has been established between the maximum wave height and the concentration of the substances. Several methods of determination have been developed. An automatic integro-differential polarograph (EP-312) was used. A dropping mercury electrode (1 drop per 1.5 to 2 sec.) served as a cathode; all measurements were taken vs. the S.C.E. in a cell with an external anode. For the reduction of pyridine and its homologues in 0.1 M CaCl<sub>2</sub>, conventional polarograms were recorded and the following half-wave potentials established—pyridine, -1.80 V;  $\alpha$ -picoline, -1.84 V;  $\beta$ -picoline, -1.86 V;  $\gamma$ -picoline, -1.91 V; 2:6-lutidine, -1.88 V; 2:4-lutidine, -1.95 V; pyridine bases (fraction 113° to 180°), -1.90 V. A new method for the determination of the maximum wave height in derivative polarography is proposed.

W. ROUBO

**2837. Use of ion exchangers in detergent analysis.** II. P. Voogt (Unilever Res. Lab., Vlaardingen, Holland). *Rec. Trav. Chim. Pays-Bas*, 1959, **78** (11), 899-912.—The procedure described in Part I (*Anal. Abstr.*, 1959, **6**, 2688) is modified and improved to reduce the time for an analysis and to avoid regeneration of the anion exchangers. After passing the ethanol-sol. part of the detergent through a column of Dowex 50-X8 (H<sup>+</sup> form) to remove cations, the active detergent in acid form (I) is adsorbed on a column of Dowex 1-X2 (acetate form) from which the sodium salts are eluted with a

0.2 to 0.3 N soln. of Na acetate in 70% ethanol. After conversion of salts into the corresponding acids, I and acetic acid are separated by ion-exclusion. The fatty acids are adsorbed on Dowex 1-X2 (OH<sup>-</sup> form) and eluted with 0.2 N KOH in 70% ethanol, whilst any urea is adsorbed on Dowex 50-X8 (H<sup>+</sup> form) from which it can be eluted with H<sub>2</sub>O (this permits N-containing cations to be separated from urea). The column arrangements are illustrated and results obtained with dodecylsulphuric acid, dodecylsulphonic acid and acyltaurines are reported and discussed. The ion-exclusion technique is probably applicable to other detergents and emulsifiers.

W. J. BAKER

**2838. Determination of surface-active agents in vinyl emulsions. I. Determination of fatty-acid soap.** Shigeyoshi Miura (Res. Lab., Toa Gosei Chem. Ind., Minato-ku, Nagoya). *J. Japan Oil Chem. Soc.*, 1959, **8** (10), 459-463.—When the method of Maron *et al.* (*Anal. Chem.*, 1952, **24**, 1068) was applied to vinyl emulsions prepared with fatty-acid soap as emulsifier, satisfactory results were obtained for styrene, vinyl chloride and vinylidene chloride but not for methyl methacrylate, butyl acrylate, methyl acrylate (I) and vinyl acetate (II). This disadvantage was overcome by using an aq. soln. of non-ionic surfactant as solvent. For I and II, which produce weak acids with dil. HCl, the results must be calibrated by measuring the weak acid content after the removal of fatty acids with CHCl<sub>3</sub>. *Procedure*—Dissolve the sample (containing 0.3 g of Na laurate) in water (150 ml), mix with polyoxyethylene nonylphenyl ether (ethylene oxide adduct) (25%, 150 ml), a known amount of 0.1 N HCl and ethanol (150 ml) and titrate conductimetrically with 0.1 N NaOH, with smooth platinum electrodes. Acidify another portion of the sample soln. (150 ml) with 0.1 N HCl and shake with CHCl<sub>3</sub> (100 ml). Centrifuge for 15 min. and titrate the aq. phase similarly with 0.1 N NaOH.

K. SAITO

**2839. New method for the quantitative determination of non-ionic surface-active compounds.** W. Kimura and T. Harada (Tech. Fac., Univ. Nagoya, Japan). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 930-934.—Earlier methods of determination of non-ionic surface-active polyalkyl compounds involved the formation of barium-tungstophosphoric acid complexes, which, however, were non-stoichiometric. The nature of these complexes has been investigated. The method is specific for surface-active polyalkyl compounds, but the non-stoichiometric behaviour was confirmed.

S. BAAR

**2840. Analytical methods in the camphor industry. I. Rapid method for the determination of camphene.** J. Błaszczewicz, K. Roczniakowa, S. Wańtuch and M. Bukala (Camphor Div., Synthetic Material Plant, Pustków). *Chem. Anal.*, Warsaw, 1959, **4** (4), 719-723.—Previously used methods for determination of camphene were found to be inaccurate and impracticable. Instead of esterification of camphene by conc. formic acid in the presence of H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) was used. The temp. was also reduced from 60° to between 15° and 20°. The isobornyl formate formed was washed with NaCl and Na<sub>2</sub>CO<sub>3</sub> soln., then dried, and its ester value was determined. The results show a coeff. of variation of  $\pm 0.91\%$ .

**II. Rapid method for the determination of isoborneol.** J. Błaszczewicz, K. Roczniakowa, S. Wańtuch and M. Bukala. *Ibid.*, 1959, **4** (4), 725-727.—In contrast to previous methods, accurate



results were obtained in the determination of iso-borneol by esterification with formic acid in the presence of  $H_2SO_4$ . The results show a coeff. of variation not exceeding  $\pm 1.75\%$ .

L. SMAKOWSKI

**2841. Micro-analysis of essential oils. II. Polarographic determination of micro quantities of carvone in vegetable material.** G. Brockelt and R. Pohloudek-Fabini (Pharm.-chem. Inst., Univ., Greifswald). *Pharm. Zentralh.*, 1959, **98** (9), 499-503.—*Procedure*—Triturate the sample (containing 0.1 to 1 mg of carvone) with sand (0.5 to 1 g) and light petroleum (boiling-range  $30^\circ$  to  $50^\circ$ ) (5 ml) and set aside in a stoppered flask for 2 hr. To the supernatant liquid add light-petroleum washings of the solid residue to give a total vol. of 11 ml. Adsorb the carvone in a 5-ml aliquot on to powdered silicic acid, which has been prepared by washing with acetone and  $H_2O$  and drying at  $105^\circ$ , and then elute it with 96% ethanol (2.5 ml). Mix the eluate with  $N LiCl-N LiOH-H_2O$  (1:1:3) (2.5 ml), deoxygenate, record the polarogram from  $-1.2 V$  vs. the S.C.E. and measure the wave height. Repeat the procedure with another 5-ml aliquot to which has been added a known vol. of a 0.1% soln. of carvone in light petroleum, and compare the wave heights. An accuracy of  $\pm 5\%$  is claimed. Results are quoted for the determination of carvone in dill fruit.

A. R. ROGERS

**2842. Determination of dyes in solution.** R. De Gori, F. Grandi and F. Santucci (Lab. Chim. Prov. Siena, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (3), 248-255.—*Procedure*—The soln. (100 ml) is treated with 5 ml of 10% acetic acid and, after removal of alcohol, the dyes are extracted on to wool, from which, after washing, the dyes are extracted with aq.  $NH_3$  soln. and identified chromatographically. A differential spectrophotometric method is given for determining Patent blue V (C.I. Acid Blue 1), indigo carmine, Brilliant black BN (C.I. Food Black 1), Sunset yellow FCF (C.I. Food Yellow 3), quinoline yellow and tartrazine. L. ZANONI

**2843. Electrophoretic separation and quantitative determination of dyestuffs.** S. Krauze and L. Piekarski (Zaklad., Bad. Srod. Spoż. Akad. Med., Warszawa). *Acta Polon. Pharm.*, 1959, **16** (5), 395-402.—Paper electrophoresis has been applied to the identification of dyestuffs used in foods and to the separation of mixtures. The apparatus is described, with diagrams. With a p.d. of 400 V and a buffer soln. of pH 12 the separation of the dyestuffs was successfully achieved; quant. determination was carried out by elution and by direct photometry on the paper. W. ROUBO

**2844. Tartrazine.** British Standards Institution (2 Park St., London, W.1). B.S. 3211:1960, 7 pp.—Limits for matter insol. in water, diisopropyl ether extract, phenylhydrazine-*p*-sulphonic acid, dye content, chloride, sulphate and metallic contaminants are included, and a method for the determination of phenylhydrazine-*p*-sulphonic acid is described. (Cf. B.S. 3210:1960.) N. E.

**2845. Improvements in the determination of holocellulose.** G. W. Holmes and E. F. Kurth. *TAPPI*, 1959, **42**, 837-840.—Replacing the 95% ethanol solvent in TAPPI standard T9m-54 with dioxan reduces the time of the experiment considerably. Extractive-free wood meal (60 to 80 mesh, 2 g) of known moisture content is chlorinated

at  $0^\circ$  and extracted first at  $0^\circ$  with dioxan and then at  $50^\circ$  with dioxan containing ethanolamine. The sample is washed once with dioxan and twice with water and the entire procedure is repeated until the sample is white after chlorination, i.e., is lignin-free. After washing with dioxan and with diethyl ether, the holocellulose is dried and weighed.

R. AICHER

**2846. Determination of the residual xanthate in regenerated cellulose threads.** B. Philipp (Dtsch. Akad. Sci., Inst. Text. Tech., Berlin). *Faserforsch. u. Textiltech.*, 1959, **10** (10), 493-495.—A works method is described for the polarographic determination, as dithiocarbamate, of the residual xanthate in regenerated cellulose threads produced by the viscose process. *Procedure*—A sample of the air-dry thread (0.5 g for thread of  $\gamma$ -value  $< 0.5$ ) is decomposed in a special apparatus, through which a slow stream of N is passed, by heating with 60 ml of 50%  $H_2SO_4$ ; the resulting  $CS_2$  passes first through a U-tube containing 20 ml of 10% aq. Cd acetate soln. (to remove  $H_2S$ ) and thence to 10 ml of a 1% (by vol.) soln. of diethylamine in 95% ethanol; to an 8-ml aliquot of this soln. is added 1 ml of 2 N LiCl, and (after de-aeration by N) the polarogram is recorded (drop time of 5 sec., temp.  $20^\circ$  and anode tension  $-2 V$ ). The dithiocarbamate content is obtained by reference to a calibration graph, prepared from standardised 0.01 M dithiocarbamate.

H. L. WHITEHEAD

**2847. Stain for the microscopical detection of damage in viscose rayon.** J. E. Ford (Brit. Cott. Ind. Res. Ass., Shirley Inst., Didsbury, Manchester 20). *Shirley Inst. Mem.*, 1959, **32**, 161-167.—A 1% soln. of Chlorazol Sky Blue FF (C.I. Direct Blue 1) in a 3% (v/v) soln. of pyridine penetrates the skin of viscose rayon at points of damage and stains the core. It can be used for the detection of commercially defective materials. N. E.

**2848. Identification of nylon and related polymers by ring paper chromatography.** J. Haslam and J. Udris (I.C.I. Ltd., Plastics Div., Welwyn Garden City, Herts., England). *Analyst*, 1959, **84**, 656-657.—The polymer is hydrolysed overnight at  $120^\circ$  with dil. HCl (Glasper et al., *Analyst*, 1957, **82**, 101) and the product is evaporated to dryness and extracted with hot ethanol. The soln. is applied to the centre of a Whatman No. 1 paper and allowed to dry. The paper is then placed between two Petri dishes, the lower containing a smaller dish with the developing solvent [ $n$ -propanol, aq.  $NH_3$  and water (6:3:1)], which is fed to the paper by means of a cotton thread. After 1.5 to 1.75 hr. the paper is removed and dried, first at room temp. and then at  $105^\circ$ . For bases and  $\epsilon$ -aminocaproic acid it is sprayed with a soln. of ninhydrin in a  $n$ -butanol-acetic acid mixture. For adipic and sebacic acids a similarly prepared paper is sprayed with a methyl red-borate buffer reagent. The  $R_F$  values found for various acids and bases are quoted. A. O. JONES

**2849. Resin acids. Analysis by mass spectrometer (as methyl esters).** C. A. Genge (Res. Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1750-1753.—An analysis of rosin acids (as methyl esters) can be carried out in about 2 hr. by using an internal standard method and a computer for solving 13 or more simultaneous equations. The mass spectrometer used is fitted with a heated inlet system operated at  $200^\circ$  and, although some isomerisation

of the more heat-sensitive compounds occurs, this causes no difficulty in the analysis. The method has been applied to a 12-component test mixture which was analysed six times over a two-week period. The average value obtained for 9 of the 12 components agreed with the known values within 10%, the other three differed by 10 to 20%. The limits of detection of the method are  $\approx \pm 1\%$ .

K. A. PROCTOR

**2850. Resin acids. Gas chromatography of their methyl esters.** J. A. Hudy (Res. Center, Hercules Powder Co., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1754-1756.—From a study of the behaviour of resin acid methyl esters on gas-chromatographic columns, with various polyesters and Apiezon grease as stationary phases at 225°, it has been established that the polyester columns offer the best means of separating and characterising the various acids. Partial isomerisation of methyl levopimarate and methyl palustrate occurs, but quant. analysis of the thermally stable acids is possible.

K. A. PROCTOR

**2851. Methods of testing plastics: Part 1: Effect of temperature.** British Standards Institution (2 Park St., London, W.1). B.S. 2782: Part 1: 1956, Amendment No. 4, 14.12.59.—The specification has been substantially revised.

**Part 5: Miscellaneous methods.** British Standards Institution. B.S. 2782: Part 5: 1958. Amendment No. 2, 31.12.59.—Addenda to the alcohol cup test for flammability are included.

**2852. Determination of methyl groups in polyethylene.** M. Rohmer (Tegernheim bei Regensburg, Nr. 171). *Z. anal. Chem.*, 1959, **170** (1), 147-152.—The curve obtained by Slowinski *et al.* (*J. Polymer Sci.*, 1956, **19**, 353), showing the ratio of the extinctions at 7.25  $\mu$  ( $\text{CH}_2$ ) and 7.30  $\mu$  ( $\text{CH}_2$ ) vs. the  $\text{CH}_2$  content per 100  $\text{CH}_2$ , is not valid at the low  $\text{CH}_2$  content of low-pressure polyethylene. A valid plot for the lower part of this curve can be obtained with the aid of a series of mixtures of low-pressure polyethylene with small additions of polypropylene.

G. BURGER

**2853. Determination of methyl groups in polyethylene.** H. Günzler (Badische Anilin- u. Soda-fabrik, Ludwigshafen (Rhein)). *Z. anal. Chem.*, 1959, **170** (1), 152-154.—The method of Bryant and Voter (*J. Amer. Chem. Soc.*, 1953, **75**, 6113), which is carried out at room temp., and requires measurement of the  $\text{CH}_2$  band only, is quicker and simpler than the method of Slowinski *et al.* (*J. Polymer Sci.*, 1956, **19**, 353), but the thickness of the sample film must be measured. A  $\beta$ -ray absorption instrument for this purpose is described. (Cf. Rohmer, *Anal. Abstr.*, 1960, **7**, 2852.)

G. BURGER

**2854. Infra-red determination of ratio of trans to cis isomers in polyesters prepared from maleic or fumaric acid.** Mu-Tong Chiang and E. G. Bobalek (Case Inst. of Technol., Cleveland, Ohio). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1959, **31**, 1287-1292.—A method is described for calculating the ratio of trans to cis isomer in polyesters prepared from  $\alpha\beta$ -unsaturated ethylenic dibasic acids and several polyhydric alcohols, from the infra-red spectra of films cast on rock-salt plates. The ratio of trans to cis isomer is  $0.217\alpha_1/\alpha_2$ , where  $\alpha_1$  is the extinction at 967  $\text{cm}^{-1}$  and  $\alpha_2$  is that at 724  $\text{cm}^{-1}$ .

D. R. DUNCAN

**2855. Quantitative infra-red measurements on poly(vinyl chloride)-plasticiser systems.** H. Luther, H. Meyer and H. Loew (Inst. f. Chem. Technol.,

Tech. Hochsch., Braunschweig). *Z. anal. Chem.*, 1959, **170** (1), 155-166.—The spectrum of PVC plasticised with dialkyl phthalates contains bands at 1728  $\text{cm}^{-1}$  for phthalate and at 1430  $\text{cm}^{-1}$  for PVC that are suitable for the determination of the plasticiser concn. Apparatus and technique for the preparation of sample films are described.

G. BURGER

**2856. Colorimetric determination of urea in urea-formaldehyde resins.** M. L. Adams and M. H. Swann (U.S. Army Ordnance Lab., Aberdeen Proving Ground, Md.). *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1959, **31**, 1247-1251.—The urea content of urea-formaldehyde resin soln., alone or in admixture with melamine resins, can be measured by the yellow colour developed with *p*-dimethylaminobenzaldehyde. The resins are first hydrolysed in methanol with HCl.

D. R. DUNCAN

**2857. Determination of the degree of condensation of urea-formaldehyde resins.** R. Květoň and A. Skálová (Sběrné Suroviny, n.p. Střelské Hostice, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (8), 446-447.—The total amount of formaldehyde is determined by decomposing the sample with  $\text{H}_3\text{PO}_4$  (40%) and steam-distilling the liberated formaldehyde with a soln. of hydroxyammonium chloride (cf. Květoň and Hanousek, *Chem. Listy*, 1954, **48**, 1537). The hydroxymethylformaldehyde or its total with free formaldehyde was determined by means of the cyanide method with the use of 0.1 to 0.3 g of the sample to which 2 N NaOH (5 ml) and N KCl (15 ml) were added, the unchanged amount of which was determined after 70 hr. by titration with 0.1 N  $\text{NH}_4\text{SCN}$  after the addition of 0.1 N  $\text{Hg}(\text{NO}_3)_2$  (15 ml) and 2 N  $\text{HNO}_3$  (6 ml) (cf. de Jong, *Brit. Abstr. C*, 1953, 509).

J. ZÝKA

**2858. Determination of adipic acid in alkyds modified with fatty drying oils.** J. Grimmer (Barvy-Laky, n.p., Prague). *Chem. Průmysl*, 1959, **9** (8), 444-445.—The method used in American and Dutch Standards for the determination of phthalic acid cannot be used for the determination of adipic acid in alkyds modified with fatty drying oils. The inaccuracy of the results can be explained by the adsorption of fatty acids on the pptd. adipate in the wash liquid as well as by the partial solubility of the adipate in the wash liquid (ether-ethanol). Reliable results were obtained with the use of the Kercow titration method (*Farben-Ztg.*, 1939, **44**, 33).

J. ZÝKA

**2859. Identification of acrylate and methacrylate polymers by gas chromatography.** E. A. Radell and H. C. Strutz (Ind. Lab., Eastman Kodak Co., Rochester, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1890-1891.—A procedure applicable to a wide range of polymers and copolymers is described. A sample of 5 mg or less is heated in a closed system in an inert gas and the pyrolysate is fed directly into a gas chromatograph. By repeating the analysis on two columns of different retention characteristics, qual. identifications can be made. Suitable stationary phases are di-*n*-decyl phthalate, diethylene glycol stearate and Dow Corning No. 550 silicone.

K. A. PROCTOR

**2860. Determination of primary amino alkyl alkoxy silane coating on glass substrates.** H. B. Bradley and D. J. Neal (Res. Lab., Linde Co., Tonawanda, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1925-1926.—The method described, which is applicable to aminosilanes of the general formula

$[H_2N(CH_2)_nSi(OR)_{4-n}]_m$  is based on the determination of total nitrogen. The sample is fused with dry KOH; the nitrogen is liberated as  $NH_3$ , which is absorbed in a boric acid soln. and subsequently titrated. The precision and accuracy are within  $\pm 10\%$ .  
G. P. COOK

**2861. Methods of testing vulcanised rubber. Parts B11 and B12. Rubber (polymer) determinations.** British Standards Institution (2 Park St., London, W.1). B.S. 903:Parts B11 and B12: 1960. 17 pp.—This specification replaces Part 4 of B.S. 903:1950. Methods are described for the calculation and for the determination of rubber (polymer) content.  
N. E.

**2862. Rubber analysis by infra-red spectroscopy.** W. Kimmer and E. O. Schmalz (VEB Chem. Werke Buna, Schkopau über Merseburg). *Z. anal. Chem.*, 1959, **170** (1), 132-147.—A procedure is described which avoids the need for comparison standards in the i.r. determination of the 1:2-, 1:4-*cis*- and 1:4-*trans*-isomers in rubber. A series of soln. at different dilutions is made from each of 3 samples. Extrapolated values for the extinction coeff. at zero concn. are calculated, and from these further calculation gives the actual extinction coeff. and the mol. concn. of each isomer.  
G. BURGER

**2863. Analysis of *cis*- and *trans*-1:4 contents of polyisoprenes by near-infra-red spectroscopy.** P. J. Corish (Dunlop Research Centre, Birmingham, England). *Spectrochim. Acta*, 1959, (8), 598-604.—Previous i.r. techniques for this analysis are shown to be non-reproducible. Satisfactory results are obtained when absorption in the near i.r. is employed. A Beckman DK2 spectrometer records the region 1.05 to 2.80  $\mu$ . Reference and synthetic samples, approx. 1% (w/v) in  $CCl_4$ , are contained in 4-cm silica or glass cells.  $E_{1\text{cm}}^{1\%}$  values for the 2.46- $\mu$  sharp combination band are plotted against known percentage of *cis*-1:4 isoprene-unit contents of rubber-gutta-percha mixtures. Alternatively, the ratio  $R = A_{2.46\mu}/A_{2.31\mu}$  is used. Dry-weight determinations of the polyisoprenes are unnecessary if the latter procedure is adopted. Unknown *cis*-1:4 isoprene-unit contents are evaluated from either of the two standard graphs.  
G. P. MITCHELL

**2864. Colorimetric determination of nitrocellulose.** E. Kälke. *Farbe u. Lack*, 1959, **65** (10), 564-565.—Conditions for the determination of nitrocellulose by the method involving saponification with aq. alkali in the presence of an org. solvent and colorimetric measurement of the di- and tri-nitro compounds formed have been examined, particularly the choice of the org. solvent and the use of a photometer or spectrophotometer for the optical procedure.  
L. A. O'NEILL

**2865. Application of ultra-violet light and diphenylamine to spot tests for explosives.** B. B. Coldwell (Crime Detection Lab., Royal Canadian Mounted Police, Ottawa, Canada). *Analyst*, 1959, **84**, 665-667.—The explosive to be examined is dissolved in acetone or hot water and separate spots consisting of 1, 2 or 3 drops, respectively, are made on filter-paper. The stained areas are examined in daylight and in u.v. light. One drop of a 1% (w/v) soln. of diphenylamine in ethanol is placed on each spot and an additional blank spot and any change in appearance is noted both before and after

exposure to u.v. light (230 to 420 m $\mu$ ) for 3 min. The results for a number of inorganic and organic nitrate explosives are tabulated.  
A. O. JONES

See also Abstracts—2607, Hydrocarbons in oils. 2610, Determination of nitrobenzene, pyridine and hydrocarbons. 2665, Germanium in ammonia liquor. 2686, N in organic compounds. 2970, 2972, Analysis of dyes. 2973, Determination of polyoxyethylene glycol esters. 3005, Benzidine in air. 3019, Organic Cl in pesticides. 3026, Nitro-meter for Dumas N determination. 3039, Determination of dye intermediates. 3040, Determination of carbonyl compounds. 3048, Determination of hydrocarbons. 3077, Anomalous i.r. absorption of OH groups. 3083, Combustion train for halogens and S. 3091, Non-aq. titration of weak acids. 3101, Mass-spectrometer inlet-system for higher hydrocarbons.

#### 4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

##### Biological fluids, animal and vegetable tissues

**2866. Diffusion of sodium and potassium in man. Measurement by chromatographic separation of the radioactive elements.** C. Sautier. *Chim. Anal.*, 1959, **41** (9), 368-373.—The rates of diffusion of sodium and potassium in man have been studied by injecting an isotonic saline soln. containing 80  $\mu$ C of  $^{24}\text{Na}$  and 250  $\mu$ C of  $^{42}\text{K}$  and subsequently determining their relative activities in plasma and urine at intervals after administration. Sodium and K are separated on Dowex 50-12X ion-exchange resin and eluted with 0.24 N and 0.9 N HCl, respectively. Results are presented for the normal subject and three abnormal cases.  
T. R. ANDREW

**2867. Titrations with quinol and similar reducing agents. XVI. Potentiometric micro-determination of gold in urine.** J. Doležal, M. Höfer and J. Zýka (Dept. Anal. Chem., Charles Univ., Prague). *Českosl. Farm.*, 1959, **8** (10), 578-579.—Procedure—To the sample of urine (50 ml) (from a patient treated with a gold-containing pharmaceutical preparation) add conc.  $HNO_3$  (4 ml) and evaporate carefully to dryness. Cool, add aqua regia (3 ml) and ignite. Repeat the ignition with 3 ml of aqua regia, dissolve the residue in  $H_2O$ , neutralise with NaOH soln. (5%) (bromocresol green as indicator), add conc. HCl (1 drop), heat, and titrate potentiometrically with 0.001 N quinol. The determination was compared with the method of standard addition and colorimetry (Natelson and Zuckermann, *Brit. Abstr. C*, 1951, 3454). Results from both methods were in good agreement for samples containing 80 to 130  $\mu$ g of Au per 100 ml.  
J. ZÝKA

**2868. Determination of aluminium and iron in plant tissue.** E. J. Rubins and G. R. Hagstrom (Storrs Agric. Exp. Sta., Univ. of Connecticut, Storrs, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (10), 722-724.—Iron is determined in plant tissue by digestion with  $HNO_3$  and  $HClO_4$ , and formation of the ferrous complex of 4:7-diphenyl-1:10-phenanthroline (bathophenanthroline) at pH 3 to 4. The complex is extracted with  $CHCl_3$ -isoamyl alcohol (10:1), and measured spectrophotometrically at 540 m $\mu$ . Aluminium is determined in the aq. phase, after the extraction of the Fe complex, by



forming the fluorescent complex of Al with 8-hydroxyquinoline, extracting it with  $\text{CHCl}_3$  at pH 4.7 to 5.1, and measuring it fluorimetrically. Quantities of Fe up to 20  $\mu\text{g}$  and Al up to 10  $\mu\text{g}$  are determined; Mn, Cu and Zn, in amounts usually found in plant tissue, do not interfere.

M. D. ANDERSON

**2869. Determination of thallium in biological material.** A. Dyfverman (Gov. Lab. for Forensic Chem., Stockholm, Sweden). *Anal. Chim. Acta*, 1959, **21** (4), 357-365.—The sample, which may consist of animal organs (25 g), cereals (10 g) or urine (100 to 150 ml), is oxidised with  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ . In the diluted combustion residue  $\text{Tl}^+$  is oxidised to  $\text{Tl}^{3+}$  with  $\text{ClO}^-$  and is then extracted with ether. Separation is thus effected from several metals that react with dithizone. The  $\text{Tl}^+$  is extracted from the ether with an aq. soln. of  $\text{SO}_2$ , the dithizone complex of  $\text{Tl}^+$  is formed at  $\approx$  pH 11 and is extracted with  $\text{CHCl}_3$ . The extinction at 510  $\text{m}\mu$  gives a measure of the  $\text{Tl}$  in the  $\text{CHCl}_3$  extract. Recoveries of 94 to 106% are obtained for 50 to 300-mg quantities of  $\text{Tl}$ , but Hg (> 1 mg), In, Cd and Bi interfere. To eliminate the effect of Hg and In, and to reduce that of Cd and Bi, the  $\text{Tl}$  is removed from the  $\text{CHCl}_3$  extract by shaking with dil. acetic acid of pH 4-6. The dithizone complex is then formed again at  $\approx$  pH 11 and is re-extracted with  $\text{CHCl}_3$ . Smaller quantities (down to 10  $\mu\text{g}$ ) of  $\text{Tl}$ , determined by the latter procedure, gave yields of 80 to 90%.

H. N. S.

**2870. Determination of chlorine, bromine and iodine in biological material by activation analysis.** H. J. M. Bowen (Wantage Radiation Lab., Grove, Berks., England). *Biochem. J.*, 1959, **73** (2), 381-384.—The method is particularly useful for determination of Br because it is more sensitive and less subject to interference by other halogens than are current methods. Solvent-extraction methods are used as much as possible because they are quicker than distillation or pptn. techniques; this is necessary because of the very short life of the radioactive isotopes produced by the neutron activation. Ashing is not attempted until the activation process is complete, after which inactive carrier is added. The ultimate limits of detection are approx.  $10^{-8}$  g for Cl,  $10^{-9}$  g for Br, and  $10^{-10}$  g for iodine.

J. N. ASHLEY

**2871. Colorimetric determination of small amounts of cobalt. Its importance in the determination of cobalt in hepatic tissues and extracts.** A. D. Ronchese and M. Mermod. *Compt. Rend.*, 1959, **249** (22), 2421-2422.—When the Co complex of 2-nitroso-1-naphthol (I) is extracted with  $\text{CHCl}_3$ , the red colour may be masked by co-extraction of excess of I or of interfering substances present in the soln. obtained from ashed hepatic material. *Procedure*—Calcine the hepatic extract or tissue until a white ash is obtained, treat with 1 to 2 ml of  $\text{HClO}_4$  and dissolve the residue in  $\text{H}_2\text{O}$ . Add I and shake with  $\text{CHCl}_3$ , then shake the organic layer with a mixture of saturated  $\text{NaHCO}_3$  soln. and  $\text{N Na}_2\text{CO}_3$  (5:6), followed by a mixture of 10% Na acetate soln. and  $\text{N HCl}$  (3:2). The red colour persisting in the organic phase is due to Co; 0.1  $\mu\text{g}$  in 0.5 ml is detectable.

P. D. FARR-RICHARD

**2872. Rapid determination of blood alcohol by diffusion oxidation in high vacuum.** H. S. Mahal (Forensic Sci. Lab., Bombay, India). *Anal. Chem.*, 1959, **31** (11), 1908-1909.—Add the sample of blood (0.5 ml) to anhydrous  $\text{Na}_2\text{CO}_3$  (1 g); distil the

ethanol *in vacuo* (a special apparatus is described) into a mixture of 0.1 N  $\text{K}_2\text{Cr}_2\text{O}_7$  (2.5 ml) and conc.  $\text{H}_2\text{SO}_4$  (10 ml) for about 1 min. and determine the unchanged dichromate iodimetrically in the usual way. The complete analysis takes 5 min. Recovery from blood containing 0.01 to 0.5% of ethanol is good. Methanol, propanol, diethyl ether, formaldehyde and chloroform are also determined, but acetone and volatile fatty acids do not interfere.

A. R. ROGERS

**2873. Influence of reducing agents in the photometric determination of phosphate in urine.** K. Schriever (Inst. f. Pharm. u. Lebensmittelchem., Univ., München). *Arch. Pharm., Berlin*, 1959, **292** (10), 555-557.—If strong reducing agents are present in the urine, the reduction of molybdophosphoric acid leads to the formation of a more strongly coloured molybdenum blue, and the Beer-Lambert law is no longer applicable. This effect can be eliminated by treatment of the sample with oxidising agents (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{KMnO}_4$  or  $\text{HNO}_3$ ). *Procedure*—Warm the sample (10 ml) with conc.  $\text{H}_2\text{SO}_4$  (2 ml) and  $\text{N KMnO}_4$  (30 ml) until the purple colour fades, cool, neutralise the soln., dilute to 200 ml and use a 1-ml aliquot for the determination of phosphate by the photometric molybdate method of Schriever *et al.* (*Dtsch. ApothZtg*, 1957, **97**, 889).

A. R. ROGERS

**2874. Rapid and sensitive electrode for continuous measurement of  $\text{pCO}_2$  in liquids and tissue.** C. H. Hertz and B. Siesjö (Dept. of Physics, Univ. Lund, Sweden). *Acta Physiol. Scand.*, 1959, **47** (2-3), 115-123.—The construction is described of an electrode in which a gas-permeable membrane of Teflon allows  $\text{CO}_2$  to diffuse from the sample into a film of water on the surface of the plane membrane of a glass electrode. A miniature calomel reference electrode is included in the assembly. The change in pH of an aq. soln. caused by dissolved  $\text{CO}_2$  is proportional to  $\log \text{pCO}_2$ , and thus the assembly can be used for the continuous measurement of  $\text{CO}_2$  concentration in fluids and tissues after calibration in saline soln. equilibrated with gas mixtures of known  $\text{CO}_2$  content.

R. A. BRENNAN

**2875. Determination of glucose in blood.** J. Felix Torres (Univ. Nacional del Sud). *Rev. Asoc. Bioquim. Argentina*, 1959, **24**, 102-108.—After removal of protein, the sample is treated with 1% diphenylamine soln. in glacial acetic acid and  $\text{HCl}$  (4:1:19) and the intensity of the blue colour so produced is measured with a green filter. The results quoted are generally lower than those given by the method of Folin and Wu, but agree well with those by the method of Nelson and Somogyi.

G. H. FOXLEY

**2876. Ultra-micro chemical analysis of blood glucose with glucose oxidase.** L. P. Cawley, F. E. Spear and R. Kendall (Dept. of Path., Wesley Hosp., Wichita, Kan., U.S.A.). *Amer. J. Clin. Path.*, 1959, **32** (2), 195-200.—A coupled enzyme system of glucose oxidase and peroxidase is used in combination with a chromogen acceptor. Glucose oxidase reagent (oxidase, peroxidase, o-dianisidine and phosphate buffer pH 7.0) (5 ml) is added to 0.025 ml of plasma at zero time; 10 min. later the reaction is stopped by the addition of 1 drop of 4 N  $\text{HCl}$  and the extinction of the mixture is measured at 400  $\text{m}\mu$ . The values are compared with those from glucose standards. Interfering substances present in haemolysed and icteric plasma are

removed by preparing a filtrate from the plasma by the method of Somogyi (*J. Biol. Chem.*, 1930, **88**, 655). The standard deviation of 20 replicated samples (200 mg of glucose per 100 ml) was  $\pm 4$  mg. P. NICHOLLS

**2877. Determination of blood urea with *p*-dimethylaminobenzaldehyde.** H. H. Brown (The Memorial Hospital, Pawtucket, R.I., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1844-1846.—Mix a 1-ml aliquot of plasma or serum with  $H_2O$  (7 ml), add 10%  $ZnSO_4 \cdot 7H_2O$  soln. (1 ml) and 0.5 *N* NaOH (1 ml), mix and filter. To 2 ml of the filtrate add 2 ml of reagent [dilute conc.  $H_2SO_4$  (5 ml) to 100 ml with a 5% soln. of *p*-dimethylaminobenzaldehyde in 95% ethanol], set aside for 10 min. and measure the extinction at 440  $m\mu$  and at 480  $m\mu$ . Treat similarly an aliquot of urea-free pooled plasma or serum and use this as a blank soln. in the spectrophotometer. The effect of temp. change on the extinction is marked and a standard urea soln. should also be measured. If  $E_{480}$  is  $> 0.1 E_{440}$  which indicates that interfering sulphonamides are present, hydrolyse the urea in a portion of the sample filtrate enzymatically, add the reagent and use this soln. as blank. The standard curve is linear at concn. of  $< 100$  mg of urea-N per 100 ml. A. R. ROGERS

**2878. Determination and stabilisation of reduced ascorbic acid in extracts from plant material.** H. T. Freebairn (Dept. of Plant Biochem., Univ. of Calif., Riverside, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1850-1851.—The use of 0.0025 *M* EDTA containing 0.3% of trichloroacetic acid as an extraction medium resulted in a high recovery of ascorbic acid from plant material as well as good stability of the extract. Metaphosphoric acid and oxalic acid soln. were inferior. The extract should be clarified by centrifugation at a low temp. A. R. ROGERS

**2879. A reproducible periodate-oxidation method for the determination of glycogen end-groups.** F. W. Fales (Emory Univ., Atlanta, Ga., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1898-1900.—The glycogen test soln. is oxidised with 0.1 *M* sodium metaperiodate for 48 hr. at about 3°, and a methyl- $\alpha$ -D-glucoside standard is run concurrently to compensate for small changes in experimental conditions which occur during the long oxidation period. The formate released from the test soln. and standard is determined by titration with standard alkali or by an iodimetric procedure. From the relative titrations of the test soln. and standard and the relative glycogen contents as determined by the anthrone method, the average chain-length can be measured. A difference in average length of 0.5 glucose unit can be distinguished with six replicate determinations. G. P. COOK

**2880. Ribitol dehydrogenase. II. Studies on the reaction mechanism. [Determination of D-ribulose.]** R. C. Nordlie and H. J. Fromm (Dept. of Biochem., Univ. of North Dakota Sch. of Med., Grand Forks, N.D., U.S.A.). *J. Biol. Chem.*, 1959, **234** (10), 2523-2531.—The method is based on the reversible reaction between the dehydrogenase and D-ribulose, which is reduced to ribitol in the presence of reduced diphosphopyridine nucleotide, which itself is converted into the oxidised form. The reaction is followed spectrophotometrically at 28° and 340  $m\mu$ . The initial concn. of D-ribulose is determined on the basis of the disappearance of reduced diphosphopyridine nucleotide, which in turn is calculated from

the change in extinction at 340  $m\mu$ . The calculated error when a 5-fold excess of reduced diphosphopyridine nucleotide is used is  $< 1\%$ .

J. N. ASHLEY

**2881. The chromatography of flavonol aglycones in a mixture of chloroform, acetic acid and water.** K. Egger (Inst. f. angew. Botan., Univ. Tübingen, Germany). *Z. anal. Chem.*, 1959, **171** (2), 96-98.— $R_F$  values are given for 15 flavonols and the influence of the position of the methoxyl and hydroxyl groups on the  $R_F$  value is discussed. The samples are chromatographed by the ascending method, with  $CHCl_3$ -acetic acid- $H_2O$  (13:6:1), on a very hard paper (No. 263 made by Macherey, Nagel & Co.). H. M.

**2882. Simplified method of countercurrent distribution for the analysis of carotenoids.** G. Nebbia and E. M. Pizzoli (Ist. di Merceologia, Univ. Bari, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (4), 364-374.—A useful fractionation of carotenoids is possible by countercurrent distribution with only ten tubes, which conveniently are 25-ml cylindrical separating-funnels. Equal volumes of hexane and 97% methanol are shaken together and 10-ml portions of the separated phases are used with 10 ml of the sample soln. Countercurrent distribution of the hexane soln. of carotenoids separates fractions containing (i) carotene plus carotenoid esters and (ii) dihydric and polyhydric carotenoid alcohols. A further countercurrent distribution of a soln. of the saponified carotenoids separates fractions containing (a) carotene, (b) monohydric alcohols and (c) dihydric and polyhydric alcohols. E. C. AFLING

**2883. Rapid method for determining the constituent components in carotenoid extracts from leaf tissue.** J. Friend and T. O. M. Nakayama (Low Temp. Res. Sta., Downing St., Cambridge, England). *Analyst*, 1959, **84**, 654-655.—The pigments are extracted with cold acetone, transferred into light petroleum in the presence of half-saturated ammonium sulphate soln. (Booth, *Analyst*, 1959, **84**, 464) and the soln. is passed through a chromatographic column of MgO and Celite 545. Elution is with light petroleum containing specified increasing amounts of acetone, so that  $\alpha$ -carotene,  $\beta$ -carotene, a violaxanthin-lutein mixture and neoxanthin are eluted in succession. The  $\alpha$ - and  $\beta$ -carotenes and neoxanthin are determined spectrophotometrically at 443, 448 and 437  $m\mu$ , respectively. The extinction of the violaxanthin and lutein mixture is measured at 400, 442 and 472  $m\mu$  before and after the addition of a drop of HCl, which converts violaxanthin into auroxanthin. The method of calculation is given. The standard error of the means of 21 replicate determinations was  $\pm 2\%$ . A. O. JONES

**2884. Paper-chromatographic analysis of long-chain fatty acids in human serum.** W. H. Hauss and G. Krickau (Med. Klinik und Poliklinik, Univ. Münster, Westphalia, Germany). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 1059-1068.—The proteins are precipitated with ethanol-ether (3:1). The ether extract is evaporated and extracted with chloroform. The chloroform is evaporated and the residue is saponified with methanolic NaOH. The unsaponifiable fraction is separated and  $\approx 175 \mu g$  in a 2% soln. in toluene is chromatographed on undecane-impregnated paper by the ascending method at 21° with glacial acetic acid-methyl cyanide-undecane (75:25:3) as developer. The

spots are revealed by treatment with cupric acetate followed by  $K_3Fe(CN)_6$  or by mercuric acetate and  $H_2S$ . The quantities present are determined by planimetry. The method is sensitive to 10  $\mu g$  of fatty acids. It was applied to the analysis of normal sera, lipaemic sera and sera from patients suffering from arteriosclerosis. In normal sera the ratio of saturated to unsaturated acids was found to be 25.5 to 74.5. In lipaemic and arteriosclerotic sera there is an increase in saturated acids.

S. BAAR

**2885. Spectrophotometric determination of small quantities of esterified fatty acids in human plasma.** G. Ivaldi and I. Macri (Ist. di Fisiol. Umana, Univ. di Genova). *Ital. J. Biochem.*, 1959, **8** (1), 35-45.—Plasma (0.5 ml) is added dropwise to ethanol-diethyl ether (1:1) in a 25-ml flask and the mixture is made up to volume with the solvent. After being shaken and set aside for 10 min. the mixture is filtered through a 5.5-cm Whatman No. 43 paper. The filtrate (5 ml) is evaporated to dryness at 60°. Diethyl ether (30 ml) and a mixture of equal parts of 0.625 *M* NaOH and 0.359 *M* hydroxyammonium chloride (0.6 ml) are added to the residue and the ether is evaporated off at 60°. Ferric perchlorate reagent (10 ml) is then added and the beaker is heated at 30° for 20 min. with occasional stirring. The extinction is then read at 530  $m\mu$  against a reagent blank. A standard curve is constructed from known soln. of triolein. *Ferric perchlorate reagent*—Iron wire (800 mg) is dissolved in 70%  $HClO_4$  (10 ml) with careful heating. The soln. is washed into a 100-ml flask with water (10 ml) and made up to volume with abs. ethanol, with cooling. This soln. is stable for 15 days at 5°. For use, the stock soln. (4 ml) and 70%  $HClO_4$  (1.2 ml) are diluted to 100 ml with anhyd. methanol.

R. A. BRENNAN

**2886. Separation of lipids by chromatography on paper impregnated with silicic acid. II. Possibilities and limitations of the method.** M. Cormier, P. Jouan and L. Girre (Fac. de Méd. et de Pharm., Rennes, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (7-8), 1037-1046.—The preparation of paper impregnated with silica and its use in the separation of lipids is described. *Procedure*—Whatman No. 1 papers (15 cm  $\times$  47 cm) are placed horizontally and soaked in a soln. prepared by diluting 750 ml of conc. aq.  $Na_2SiO_3$  (*d*, 1.38 to 1.40) to 1 litre; they are then turned over and soaked the other way up, and finally pressed between sheets of Durieux filter-paper. The Whatman papers are then plunged twice on each side in 5 *N* HCl, and washed for 30 min. in running water, and then three times for 10 min. in distilled water, and dried in air. The papers must be kept flat for several weeks before use. Lipids are chromatographed with diethyl ether-light petroleum-heptane (4:25:25) by the ascending technique at 27° for 5-5 hr. Unsaturated fats are revealed with 0.1% Sudan black soln. Cholesterol is revealed by the green colour produced on treating the paper with acetic anhydride containing 20% of  $H_2SO_4$ . To reveal cholesteryl oleate and palmitate the reagent must contain 25% of  $CHCl_3$ . Fatty acids are detected with 0.1% aq. Cu acetate soln.  $R_f$  values are quoted, and the effect of varying the conditions is studied. The method is applied to the neutral fats of blood serum.

E. J. H. BIRCH

**2887. Fractionation of a leucocidin from *Staphylococcus aureus*. [Determination of leucocidin.]** A. M. Woodin (Sir William Dunn Sch. of Path., Univ. of Oxford, England). *Biochem. J.*, 1959, **73**

(2), 225-237.—An assay method, suitable for routine use, is based on the ability of leucocidin to prevent the reduction by macrophages of 2:6-dichlorophenolindophenol to a colourless compound in the presence of KCN. Serially diluted soln. of leucocidin are incubated with macrophages, the dye and KCN are added, and incubation is continued until a clear distinction can be made between those soln. which are blue (in which the macrophages are dead) and those which are colourless (where the dye has been reduced by the living cells). The method is useful for the direct determination of the leucocidin activity of a soln. or its anti-body-combining power.

J. N. ASHLEY

**2888. Excretion of allantoin and its derivatives in the rat and in man. Determination of allantoin by chromatography.** R. Crokaert (Lab. de Biochem., Fac. de Méd., Univ. Libre de Bruxelles, Belgium). *Bull. Soc. Chim. Biol.*, 1959, **41** (7-8), 1001-1016.—*Procedure*—Urine (5 ml) is passed through a column of Dowex 50-X8 ( $H^+$  form) (5 cm  $\times$  2 cm), which removes urea. The percolate, with 20 ml of wash water, is evaporated to dryness, the residue is taken up in 5 ml of water, and, with rat urine, an aliquot of 0.2 to 1 ml is taken; with human urine the residue is taken up in 1 to 2 ml of water and used completely. After acidifying to pH 1 to 1.5 the soln. is passed through a column of Dowex 50-X8 (50 cm  $\times$  1 cm) buffered to pH 2.5 with a citrate buffer, which is also used to elute the column. The fractions obtained are analysed for substances that react with diacetyl monoxime by the Koritz and Cohen method as modified by Schram and Crokaert (*Ibid.*, 1957, **39**, 561), reading the extinction at 550  $m\mu$  after 40 min. in a water bath at 25°. Alternatively, the allantoin is determined by alkaline hydrolysis to allantoic acid, which is then hydrolysed in acid to glyoxylic acid. This is condensed with phenylhydrazine and oxidised with  $K_3Fe(CN)_6$  to give a red colour, read at 525  $m\mu$  (Christman *et al.*, *J. Biol. Chem.*, 1944, **155**, 161). Fractions giving positive reactions can be recombined and chromatographed on paper with *n*-butanol-water-acetic acid (5:4:1) or phenol satd. with water as mobile phase, and detected with 4% *p*-dimethylaminobenzaldehyde soln. in *N* HCl. Four separate products are observed, including allantoin, allantoic acid, and urea formed in the course of chromatography.

E. J. H. BIRCH

**2889. Determination of hexosamines as phenylthiocarbamoyl derivatives.** J. Sjöquist (Dept. of Physiol. Chem., Univ. Lund, Sweden). *Ark. Kemi*, 1959, **14** (4), 323-325.—The method for the determination of N-terminal amino acids as phenylthiohydantoin derivatives (*cf.* *Anal. Abstr.*, 1958, **5**, 1628; 1960, **7**, 2896) has been modified. *Procedure*—The soln. (100  $\mu l$  = 100  $\mu g$  of hexosamine) is evaporated to dryness, treated with 0.1 ml of buffer soln. at pH 10.1 (2 ml of 2 *N* acetic acid, 1.2 ml of triethylamine and water to 25 ml) and 0.1 ml of phenyl isothiocyanate soln. (0.6% by vol. in acetone) and maintained at 40° for 1 hr., then evaporated to dryness *in vacuo* over  $P_2O_5$ . The residue is dissolved in 0.1 ml of 90% acetic acid, and aliquots (5, 10 and 20  $\mu l$ ) of the soln. are applied to Whatman No. 1 paper, and chromatographed with heptane-*n*-butanol-75% formic acid (40:30:9). The paper is dried at 100° for 30 min., then the spots are located under u.v. light, cut out and eluted with 95% ethanol (2 ml) and the extinctions are read at 240  $m\mu$ . No separation of glucosamine and galactosamine was achieved by the procedure described.

S. BAAR



**2890. Investigation into the titration assay of amino acids. I; II.** S. Lewin (Phys. Chem. Lab., S.-W. Essex Tech. Coll., London). *Lab. Practice*, 1959, 8 (9), 292-294; (10), 330-332.—Volumetric alkalimetric titrations of amino acids in aq. soln. are studied, with special reference to the Sørensen formaldehyde procedure. The effects of formaldehyde purity and concn. are discussed and the necessity for preventing the growth of micro-organisms in the amino-acid soln. is stressed. The addition of toluene as a bacteriostatic agent is recommended, and some necessary precautions are described.

R. A. BREMAN

**2891. Analysis of amino acids using an automatic technique.** I. E. Taylor and M. M. Marsh (Anal. Res. Dept., Eli Lilly and Co., Indianapolis, Indiana, U.S.A.). *Amer. J. Clin. Path.*, 1959, 32 (4), 393-396.—A commercial automatic analyser is modified to give optimum conditions for the reaction of ninhydrin with amino acids. The colour reagent is introduced into the reaction stream by a displacement technique. Reproducible results are obtained.

P. NICHOLLS

**2892. A modified high-voltage electro-chromatographic method for amino acids.** P. Masłowski (Dept. of Biochem., Sch. of Agric., Olsztyn, Poland). *Chem. Anal., Warsaw*, 1959, 4 (3), 611-618.—The separation of 17 amino acids on one sheet of chromatographic paper (S. & S. 2043b) is based on electrophoresis for 90 min. at 60 V per cm in acetate buffer at pH  $\approx$  2. The electropherogram is then fastened to a strip of Whatman No. 1 paper, rolled into a cylinder and developed for 16 hr. at 20°, in a direction perpendicular to the direction of electrophoresis. A mixture of *sec*-butyl alcohol, formic acid and water (15:3:2) is used and the spots are located with ninhydrin.

W. B. MIAKOWSKI

**2893. Detection of 2:4-dinitrophenylamino acids on paper chromatograms.** A. H. Maddy (Dept. Zool., Roy. Holloway Coll., Englefield Green, Surrey, England). *Nature*, 1959, 184 (Suppl. No. 18), 1397-1398.—Two colour reactions are described. (i) The chromatogram is first sprayed with 1.5% (w/v)  $\text{TiCl}_3$  soln. in 0.5 N HCl and heated for 15 min. at 60°, then sprayed with a mixture (1:2) of 0.33% *p*-dimethylaminobenzaldehyde soln. in 50% HCl and ethanol. The 2:4-dinitrophenyl amino acids react to give yellow-orange spots which fade rapidly but re-appear in 10 to 15 hr. Since nitro compounds give the reaction only after reduction, they can be distinguished from aromatic amines, pyrrole and its derivatives. (ii) The chromatogram is dipped into 8% (w/v) KCN soln. and heated for 2 min. at 90°. 2:4-Dinitrophenyl derivatives produce red-violet spots. The sensitivity is 2 to 3  $\mu\text{g}$ . The reaction is claimed to be specific.

S. BAAR

**2894. The infra-red spectra of some DNP- $\alpha$ -amino acids.** F. Friedberg and M. S. O'Dell (Howard Univ. Med. School, Washington, D.C.). *Canad. J. Chem.*, 1959, 37 (9), 1469-1477.—Data are reported in the region 5000 to 625  $\text{cm}^{-1}$  for the 2:4-dinitrophenyl derivatives of 19 amino acids.

N. E.

**2895. Chemical method for the determination of cysteamine in biological materials.** P. Lelièvre (Lab. d'Anat. Path., Univ., Liège, Belgium). *Bull. Soc. Chim. Biol.*, 1959, 41 (9-10), 1207-1219.—Mixtures of cysteamine (2-aminoethanethiol) (I)

and its disulphide (cystamine) (II) are determined polarographically as their  $\text{Co}^{II}$  complexes ( $E_1 = -1.55$  V vs. the S.C.E.). For pure soln., a mixture of N  $\text{NH}_4\text{Cl}$  (0.5 ml), 0.008 N  $\text{CoSO}_4$  (1 ml), N aq.  $\text{NH}_3$  (0.5 ml) and 0.05% gelatin soln. (0.5 ml) is treated with the test soln., made up to 5 ml with water, and polarographed. The complexes are formed by combination of  $\text{Co}^{II}$  with the -SH group of I and the -S-S- group of II; treatment with iodoacetic acid blocks the former, but not the latter, so that subsequent polarography measures II alone, I being then obtained by difference. The height of the wave is proportional to the concn. within certain limits (not stated), and it is claimed that 0.01  $\mu\text{g}$  of I per ml can be determined with a precision of  $\pm$  3%. The  $\text{Co}^{II}$  complexes of cysteine (III) and cystine (IV) give polarographic waves that are identical with those of I and II; III and IV can be removed by passage through a column of Amberlite IRA-400 (OH<sup>-</sup> form), previously treated with a 1% aq. soln. of ethanethiol (V). This retains III and IV; I and II are eluted with V followed by water. The eluate is evaporated to dryness *in vacuo* in the presence of HCl, and the residue is dissolved in water and polarographed as described above; 50  $\mu\text{g}$  of I was quant. recovered from admixture with 20 mg of III. Procedures are described for the determination of I and II in blood and tissues, which involve pptn. with abs. ethanol. Interfering substances are retained on the resin column, but only a part of the I appears in the ethanolic soln., the remainder being recovered from the ppt. after hydrolysis with HCl and passage of the soln. through the ion-exchange column.

S. BAAR

**2896. Determination of N-terminal amino acids in peptides.** J. Sjöquist (Dept. Physiol. Chem., Lund Univ., Sweden). *Ark. Kemi*, 1959, 14 (4), 291-293 (in English).—The determination of N-terminal amino acids in peptides as phenylthiohydantoin derivatives by the method described by Edman (*Acta Chem. Scand.*, 1950, 4, 277) leads to decreases in yield at every step in the degradation. This had been ascribed to the formation of an intermediate 2-aminophenyl-5-thiazolinone derivative, but the correct explanation was found in the incompleteness of the reaction. A test experiment with 4 mg of insulin is described. The original method was used, but the insulin was allowed to react thrice with phenyl isothiocyanate. The third treatment still gave yields of 90% and 87% of the appropriate amino acids.

S. BAAR

**2897. Comparison of three methods for the quantitative evaluation of paper electropherograms of blood serum obtained by electrophoresis.** J. Kowalczyk (Centr. Chem. and Bacteriol. Lab., State Clinical Hosp., Med. Acad., Gdańsk). *Chem. Anal., Warsaw*, 1959, 4 (3), 589-602.—The main factors affecting the following three methods have been studied on electropherograms of normal blood serum:—(i) elution of the whole stained spots, and photometry of the coloured eluates; (ii) cutting the electropherogram into strips, followed by elution of the strips, absorption measurements on the eluates, plotting an absorption curve, and measurements of the areas under the peaks; (iii) direct absorption measurements on the electropherogram, followed by plotting of the absorption curve and measurement of the areas under the peaks. The results indicate that method (i) is the most reliable.

W. B. MIAKOWSKI

2898. Agar electrophoresis of normal soluble proteins in guinea-pig liver. I. Goranov, Y. Todorov, X. Skatshokova, M. Hlebarova and P. Kuzmanova (Postgrad. Med. Training Inst., Sofia, Bulgaria). *Nature*, 1959, **184** (British Association Suppl.), B.A. 64-65.—The liver is ground with sand, 0.7% NaCl soln. (1 to 3 ml) is added, the mixture is stored in a refrigerator for 24 hr. and then centrifuged at 6000 r.p.m. for 2 to 3 hr. The aq. layer beneath the superficial lipid layer is used for the electrophoresis. The method employed is a slight modification of Grabar's technique with a barbitone - Na acetate buffer soln. (pH 8.6,  $\mu = 0.06$ ) and a p.d. of 180 to 200 V applied for 5 hr. Staining is with Amido black 10B (C.I. Acid Black 1). Thirteen well-defined fractions were established.

H. F. W. KIRKPATRICK

2899. Sialic acid and the specificity of the periodic acid - Schiff's fuchsine reaction applied to electrophoresis on paper, with special reference to orosomucoid. J. Montreuil and G. Biserte (Lab. Chim. Biol., Fac. de Méd. et de Pharm., Lille, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (7-8), 959-973.—The determination of colour developed on paper electropherograms of hydrolysed and unhydrolysed orosomucoid by periodic acid oxidation and treatment with Schiff's reagent (Koiv and Grönwall, *Scand. J. Clin. Lab. Invest.*, 1952, **4**, 244) is investigated. By controlled hydrolysis with 0.01 N  $H_2SO_4$  at 100° followed by electrophoresis, it is shown that a new species is formed which gives a lighter colour with the reagent; hydrolysis is complete in 45 min., but further slight denaturation takes place at 60 min. Dialysis of orosomucoid hydrolysed with acid or enzymes, and investigation of the oses, osamines and sialic acid in the undialysable fraction shows that only the sialic acid is split off, and its content falls by 80% compared with that in the unhydrolysed material; the lost sialic acid is recovered in the dialysable fraction. These results are confirmed by electrophoresis. It is shown that a longer oxidation with periodic acid is required before a colour is developed with Schiff's reagent when the mucoid is thus hydrolysed. The effect of these phenomena on analytical applications is discussed.

E. J. H. BIRCH

2900. Quantitative separation of sphingomyelins. Application to the study of the renewal of sphingomyelin *in vivo*. R. Bieth, G. Rebel and P. Mandel (Inst. de Chim. Biol., Fac. de Méd., Strasbourg, France). *Bull. Soc. Chim. Biol.*, 1959, **41** (7-8), 1027-1035.—*Procedure*—The lipids from tissue are extracted several times in 20 times the sample weight of  $CHCl_3$  - methanol (2:1) and filtered. The extracts are washed with water and  $CHCl_3$  - methanol - water (8:4:3) (upper layer). Methanol is added to homogenise the extract. The soln. is evaporated to dryness and dissolved in benzene and the non-lipid matter is centrifuged off. The soln. is treated at 0° with excess of acetone containing a few drops of satd. ethanolic  $MgCl_2$  soln. and the resulting ppt. is separated by centrifuging and dissolved in benzene; the soln. is adsorbed on a column of Merck silica (30 to 35 g of silica mixed with Hyflo-Supercel for 30 mg of lipid P). The column is washed with 50 to 100 ml of  $CHCl_3$  and extracted with mixtures of  $CHCl_3$  - methanol; the lecithin - sphingomyelin fraction is eluted with 200 ml of the 3:7 mixture and 250 ml of methanol. This eluate is evaporated, saponified with 0.4 N ethanolic KOH for 2 hr. at 37° and the saponified matter is dissolved in water. The unsaponifiable residue is extracted with light petroleum and is

shown by chromatography and the use of  $^{32}P$ -labelled sphingomyelin to be pure sphingomyelin. The application to the investigation of sphingomyelin metabolism is described.

E. J. H. BIRCH

2901. Chemistry of the Liebermann - Burchard colour reaction for sterols and triterpenes and their esters. C. H. Brieskorn and H. Herrig (Inst. f. Pharm. u. Lebensmittelchem., Univ., Münster i. Westf.). *Arch. Pharm., Berlin*, 1959, **292** (10), 485-496.—The significance of chemical structure with respect to the development of colour in the Liebermann - Burchard reaction is discussed, with many examples.

A. R. ROGERS

2902. Comparison of the methods of Bloor and Schoenheimer - Sperry in the estimation of cholesterol in serum. M. J. Duffie and J. L. Guravich (Dept. of Path. and Med., Lancaster Hosp., St. John, N. Brunswick, Canada). *Amer. J. Clin. Path.*, 1959, **32** (1), 92-96.—The method of Bloor (*J. Biol. Chem.*, 1916, **24**, 227) is as accurate as a modification of that of Schoenheimer and Sperry (*Ibid.*, 1950, **187**, 97) and gives readings which are 1.044 times as large. In addition, the former method is simple and rapid.

P. NICHOLLS

2903. Oscillographic polarography of steroids. II. Cholesteryl esters. V. Morávek (Biochem. Inst., Fac. Natural Sci., Masaryk Univ., Brno, Czechoslovakia). *Publ. Fac. Sci. Univ. Masaryk*, 1958, (398), 389-396 (in English).—Oscillograms of pure steroids in an isopropyl alcohol - HCl solvent with the dropping electrode and the streaming electrode are described. For the test the steroid soln. in isopropyl alcohol is mixed with 5 M HCl (0.2 ml) and sufficient isopropyl alcohol to make a total vol. of 1 ml. The concn. of steroid is proportional to the wave height or the quadrant area. Differences from the basic oscillogram of cholesterol increase with increasing chain length of the esterifying fatty acid.

III. Assay of steroids and their structural relations. V. Morávek. *Ibid.*, 1959, (400), 23-26 (in English).—The method described above is applied to oestradiol, progesterone, deoxycorticosterone acetate, cortisone acetate, equilin, equilenin, androstenedione and 14 other steroids. The results are described and the effect of substituent groups on the oscillograms is discussed.

H. F. W. KIRKPATRICK

2904. Use of Porter - Silber and Schiff's reagents as spot tests for steroids applied on paper and their application to the study of rat adrenal lipids. M. K. Birmingham (Allen Mem. Inst. of Psychiat., McGill Univ., Montreal, Canada). *Nature*, 1959, **184** (British Association Suppl.), B.A. 67-68.—A bright yellow colour appears instantly with  $C_{21}$  aldehydes and their acetates, or in 1 to 2 hr. with steroids containing the dihydroxyacetone side-chain and their acetates, when a paper region containing a minimum of 2  $\mu g$  per sq. cm of the steroid is passed through Porter - Silber reagent (25 ml of  $H_2O$ , 41 ml of conc.  $H_2SO_4$ , 34 ml of ethanol and 43 mg of phenylhydrazine hydrochloride). Corticosterone, 17-hydroxyprogesterone and other steroids gave no colour.  $C_{21}$  aldehydes freshly prepared by oxidation with cupric acetate may be detected by Schiff's reagent. The Porter - Silber spot test is applicable to the detection of chromogens in lipid extracts of biological fluids.

H. F. W. KIRKPATRICK

2905. Liquid scintillation counting for  $[^{14}C]$ -steroids. S. R. Stitch (M.R.C. Radiobiol. Res. Unit, A.E.R.E., Harwell, Berks., England). *Bio-*

*chem. J.*, 1959, **73** (2), 287-292.—The assay of [ $^{14}\text{C}$ ]steroids with the Ekco type N 612 liquid scintillation counter is described. Among the advantages of the method are the high solubility of the steroids in the organic phosphor, the high over-all efficiency, and the convenience. With the Ekco instrument 65 to 69% efficiency is attained for the detection of  $^{14}\text{C}$  based on [ $^{14}\text{C}$ ]naphth-2-ol and [ $^{14}\text{C}$ ]testosterone. The method is highly reproducible; strong quenching of the scintillation is not caused by any of 25 steroids examined, but some quenching is observed with certain compounds, especially oestrone and equilenin. Other methods for the determination of  $^{14}\text{C}$  are discussed.

J. N. ASHLEY

**2906. Estimation of  $\text{C}_{19}$   $\Delta^4$ -3-oxosteroids in human urine.** A. Brancaccio, B. D'Alessandro, F. Galdiero and G. Jacono (Ist. di Semeiotica Medica, Univ. Napoli). *Ital. J. Biochem.*, 1959, **8** (1), 3-8 (in English).—The free and conjugated steroids in a 24-hr. urine sample are extracted with diethyl ether at pH 7 and pH 1, respectively; the ether extracts are washed with 10%  $\text{NaHCO}_3$  soln. and water, and freed from  $\text{C}_{21}$  compounds by chromatography on a column of Florisil, eluting with ether or  $\text{CHCl}_3$  containing 2% of methanol. The eluates are dried and dissolved in methanol and an aliquot ( $\approx 20$  ml of urine) is placed in each of two test-tubes and the methanol is evaporated off. To one tube is added isoniazid soln. (50 mg dissolved in 100 ml of ethanol containing 0.625 ml of conc.  $\text{HCl}$  per litre) (2.5 ml), and to the other acid ethanol (2.5 ml). After setting aside the tubes for 1 hr. at  $28^\circ$  the extinction is read at 380  $\text{m}\mu$ .

R. A. BRENNAN

**2907. Estimation of  $\text{C}_{21}$   $\Delta^4$ -3-oxosteroids in human urine.** A. Brancaccio, B. D'Alessandro, R. De Luca and G. Jacono (Ist. di Semeiotica Medica, Univ. di Napoli). *Ital. J. Biochem.*, 1959, **8** (3), 143-148 (in English).—The determination of  $\Delta^4$ -3-oxosteroids colorimetrically with isoniazid was compared with the Porter and Silber and the blue tetrazolium methods. The free and conjugated steroids were separated by chromatography on a column of Florisil and both types gave a positive reaction with isoniazid. The results by the Porter and Silber and blue tetrazolium methods, but they agree with those obtained by biological methods.

R. A. BRENNAN

**2908.  $16\alpha$ -Hydroxysteroids. II. Partition chromatography of triamcinolone and related steroids.** L. L. Smith, T. Foell, R. De Maio and M. Halwer (Chem. Process Improvement Dept., Lederle Labs, American Cyanamid Co., Pearl River, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (9), 528-532.—Six Bush-type solvent systems are recommended for descending chromatography on Whatman No. 1 paper. The system benzene-acetone- $\text{H}_2\text{O}$  (2:1:2) is most generally useful for qual. analysis. Detect the steroids by examination under u.v. light, by means of the isoniazid reagent of Smith and Foell (*Anal. Abstr.*, 1959, **6**, 3142) and of alkaline blue tetrazolium spray. For the quant. analysis of 100- $\mu\text{g}$  quantities, use the system benzene-ethanol- $\text{H}_2\text{O}$  (2:1:1); after development, dry the chromatogram, elute the zones with hot ethanol and measure the extinction at 239  $\text{m}\mu$ . For the more accurate quant. analysis of 3-mg quantities, use column chromatography on Celite 545 with dioxan-cyclohexane- $\text{H}_2\text{O}$  (5:2:1, 5:3:1, or 5:4:1) as solvent system and measure the eluted fractions

by the physico-chemical methods described previously (Smith and Halwer, *Anal. Abstr.*, 1960, **7**, 1169).

A. R. ROGERS

**2909. Simplified method for the simultaneous determination of 17-oxosteroids, dehydroepiandrosterone and 17-hydroxycorticosteroids in serum.** E. L. Saier, E. Campbell, H. S. Strickler and R. C. Grauer (W. H. Singer Mem. Res. Lab., Alleghany Gen. Hosp., Pittsburgh, Pa., U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1959, **19** (9), 1162-1173.—17-Hydroxycorticosteroids are extracted from serum with  $\text{CHCl}_3$ , chromatographed by the method of Nelson and Samuels (*J. Clin. Endocrin.*, 1952, **12**, 519; *Ibid.*, 1953, **13**, 1280), and assayed by the method of Silber and Porter (*J. Biol. Chem.*, 1954, **210**, 923). The aq. liquid from the  $\text{CHCl}_3$  extraction is acidified and extracted with ethyl acetate; the combined extracts are incubated at  $37^\circ$  for 24 hr. to hydrolyse the conjugates, and the steroids are purified by column chromatography on Florisil, followed by solvent partition. The total 17-oxosteroids are assayed by an adaptation of the Zimmermann reaction, and dehydroepiandrosterone by its colour reaction with ethanol- $\text{H}_2\text{SO}_4$ .

H. F. W. KIRKPATRICK

**2910. Separation of free 17-hydroxysteroids from steroid conjugates [in urine] by column chromatography.** A. Brancaccio, B. D'Alessandro, F. Galdiero and G. Jacono (Ist. di Semeiotica Medica, Univ. di Napoli). *Ital. J. Biochem.*, 1959, **8** (3), 139-142 (in English).—A butanol extract of the urine is evaporated to dryness and re-dissolved in methanol (2 ml). The methanolic soln. is poured on a column of Florisil (1 cm  $\times$  7 cm) and eluted with methanol- $\text{CHCl}_3$  (7:13) to give the free steroids and with methanol-water (1:1) to give the conjugated steroids.

R. A. BRENNAN

**2911. Estimation of dehydroepiandrosterone in urine.** K. Fotherby (Clin. Endocrin. Res. Unit (M.R.C.), Univ. of Edinburgh, Scotland). *Biochem. J.*, 1959, **73** (2), 339-343.—The method is based on the hydrolysis of the sulphate of the steroid when urine, without acidification, is heated at  $100^\circ$  for 6 hr. This hydrolysis procedure is specific for the conjugates of  $3\beta$ -hydroxy- $\Delta^4$ -steroids. Approx. equal amounts of dehydroepiandrosterone and  $6\beta$ -hydroxy-3:5-cycloandrostan-17-one are present after the hydrolysis in the absence of acid. They are eluted together after chromatographic separation from other products, and the dehydroepiandrosterone is determined by the Pettenkofer method as modified by Fotherby (*Ibid.*, 1958, **69**, 596).

J. A. ASHLEY

**2912. Determination of aldosterone in urine.** V. R. Mattox and M. L. Lewbart (Sect. of Biochem., Mayo Clinic, Rochester, Minn., U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1959, **19** (9), 1151-1161.—Urine is hydrolysed by adjusting the pH to 1.0 with conc.  $\text{HCl}$  and setting it aside at room temp. for 18 hr. The steroids are extracted with  $\text{CHCl}_3$  and the aldosterone is separated by chromatography with (i) formamide- $\text{CHCl}_3$ , (ii) formamide-butanol- $\text{H}_2\text{O}$  and (iii) ethyl acetate-toluene-benzene- $\text{H}_2\text{O}$ . The amount is determined in the final chromatogram with alkaline blue tetrazolium soln.

H. F. W. KIRKPATRICK

**2913. Chemical determination of aldosterone in urine.** C. Sobel, R. J. Henry, O. J. Gorlup and M. Rudy (Bio-Science Lab., 12330 Santa Monica Blvd., Los Angeles, Calif., U.S.A.). *J. Clin.*



**Endocrin. & Metabolism**, 1959, 19 (10), 1302-1311.—The proposed method comprises combined acid hydrolysis and  $\text{CHCl}_3$  extraction, column chromatography on silica gel, paper chromatography in two successive systems, acetylation, paper chromatography in a third system, and fluorimetry directly on the paper. H. F. W. KIRKPATRICK

**2914. Modification of the method of Somogyi for the determination of amylase in biological materials.** E. Levin. *Rev. Asoc. Bioquím. Argentina*, 1959, 24, 79-88.—The original method of Somogyi (*J. Biol. Chem.*, 1938, 125, 399) is modified by pptg. the proteins in the sample by treatment with  $\text{Ba}(\text{OH})_2$  and  $\text{ZnSO}_4$  before treatment with alkaline copper soln. This permits the reduction of the copper to be measured photometrically.

G. H. FOXLEY

**2915. Colorimetric estimation of the elastolytic activity of pancreatic extracts.** G. Rancati, P. Marrama, C. Ferreri and B. Bonati (Ist. di Clin. Med. Gen. e Terap. Med., Univ. di Modena). *Ital. J. Biochem.*, 1959, 8 (2), 71-76 (in English).—Purified elastin prepared from horse ligamentum nuchae and stained with orcein, is incubated with the elastase preparation under test, and the amount of orcein-stained elastin dissolved is determined spectrophotometrically. **Procedure**—Orcein-stained elastin (20 mg) is placed in each of a series of centrifuge tubes and to each tube is added glycine buffer (I) (pH 8.93) (1 ml) and water (1 ml). The tubes are warmed to 37° and, after 5 min., increasing amounts of the sample, dissolved in 1 ml of I, are added; I only is added to the blank. The contents of the tubes are stirred magnetically, and after 20 min. the reaction is stopped by adding 0.7 M phosphate buffer (II) (pH 6) (2 ml) to each tube. After centrifuging, the extinctions of the supernatant liquids are read at 590 m $\mu$ . A standard curve is prepared by adding I (1 ml), water (1 ml) and elastase soln. (1 ml) to increasing amounts of orcein-stained elastin (2 to 20 mg) and incubating at 37° with stirring until dissolution of the elastin is complete; II (2 ml) is then added to each tube and the extinction is read at 590 m $\mu$ . Since the staining power of elastin is variable, each new batch of substrate should be tested.

R. A. BRENAN

**2916. Rapid and sensitive method for the determination of xanthine oxidase activity using the oxygen electrode.** M. Bacila and G. G. Villela (Biochem. Lab., Inst. Biol., Curitiba, Brazil). *Nature*, 1959, 184 (Suppl. No. 18), 1394-1395.—Xanthine oxidase at low concn. initiates the aerobic oxidation of  $\text{Na}_2\text{SO}_3$  in the presence of hypoxanthine, and the oxygen consumption occurring during this reaction can be measured conveniently with an oxygen electrode (cf. Chance, *Harvey Lect.*, 1953-1954, Ser. 49, 145), polarised at -0.6 V. The xanthine oxidase activity of dialysed rat-liver homogenates was measured in this way. The homogenate (0.4 ml) containing 0.2 to 0.8 mg of protein nitrogen was diluted with 1.4 ml of phosphate buffer (pH 7.8), 0.01 ml of 0.1 M  $\text{Na}_2\text{SO}_3$  and 0.1 ml of  $5 \times 10^{-5}$  M hypoxanthine were added, and the oxygen uptake was measured by means of the electrode and graphically recorded in  $\mu\text{moles per sec.}$  S. BAAR

See also Abstracts—2657, Counting of  $^{14}\text{C}$ . 2767, Determination of aldoses. 2768, Detection of sugars and polyols. 2769, Identification of sugar phosphates. 2770, Determination of reducing

sugars. 2771, Determination of methyl arabinosides. 2776, Determination of gluconic and citric acids. 2789, Separation of phosphoric acid esters. 2808, Determination of pentosans. 2927, Determination of adenine. 2965, Carotene determination. 2976, Inulin in chicory. 3008, Fulvic acids in water. 3029, Automatic titration of  $\text{Cl}^-$  in biological fluids. 3076, Errors in i.r. absorption of sugars. 3099, Measurement of  $^{14}\text{C}$ .

#### Pharmaceutical analysis

**2917. Ultra-violet spectrophotometric micro-determination of alkaloids as tetraphenylborides. I. Establishment of the method and description of the spectra.** J.-A. Gautier, J. Renault and J. Rabiant (Lab. de Chim. Org., Fac. de Pharm., Paris). *Ann. Pharm. Franç.*, 1959, 17 (6), 401-408.—The u.v. spectra of the tetraphenylborides of a number of alkaloids are determined in methyl cyanide soln. The u.v. spectrum of K tetraphenylboron itself is determined; no absorption is shown at wavelengths > 290 m $\mu$ . Alkaloids can be divided into three classes, viz. (i) those (e.g., atropine, genatropine, pilocarpine, hyoscyne and sparteine) in which the alkaloid does not absorb beyond 260 m $\mu$  and the determination is effected by means of the tetraphenylboron spectrum; it is necessary to eliminate ions (e.g.,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$  and  $\text{Hg}^{++}$ ) that give water-insol. tetraphenylborides, and it is impossible to differentiate the alkaloids; (ii) those (e.g., codeine, codeine, morphine, pholcodine, cocaine and strychnine) with characteristic absorption spectra between 260 and 290 m $\mu$ ; and (iii) those (e.g., boldine, brucine, eserine, geserine, papaverine and procaine) with characteristic spectra at wavelengths > 290 m $\mu$ .

**II. Application to the control of pharmaceutical preparations.** J.-A. Gautier, J. Renault and J. Rabiant. *Ibid.*, 1959, 17 (7-8-9), 491-497.—**Procedure**—To a sample of 1 to 2.5 mg of alkaloid in 10 to 30 ml of water are added 2 drops of 10% acetic acid (to pH  $\approx$  5), 2 drops of 10% aq.  $\text{AlCl}_3$  soln. (as a flocculant) and a 2- or 3-fold excess of 0.2% aq. Na tetraphenylboron soln. The ppt. is separated and dissolved in methyl cyanide and, after making up the soln. to volume (25 or 50 ml) with methyl cyanide, the extinction is determined at an appropriate wavelength (see Part I, above). As an example of the determination of alkaloids in complex media, the determination of codeine in official bromoform syrup is described. The alkaloid is extracted from the preparation with  $\text{CHCl}_3$ , in the presence of 5 ml of 10% aq.  $\text{Na}_2\text{CO}_3$  soln. and re-extracted into 2% aq. acetic acid for pptn. with Na tetraphenylboron. A mixture of two alkaloids absorbing at sufficiently different wavelengths in the u.v. can be separately determined simultaneously.

E. J. H. BIRCH

**2918. Microchemical identification of some alkaloids, barbiturates, sulphonamides and new synthetic drugs.** II. T. P. A. van der Wegen (Farm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1959, 94 (21), 685-701.—Microchemical reactions are described for benzoylcocaine, cocaine hydrochloride, allobarbitone, ethylmorphine hydrochloride, dipiperon hydrochloride, orphenadrine hydrochloride, ecgonine, ephedrine hydrochloride, rac-ephedrine hydrochloride, sulphasomidine, benzamine hydrochloride, oxycodone, eupaverine hydrochloride and hexobarbitone. (46 illustrations.)

M. J. MAURICE

**2919. Determination of morphine in opium.** A. B. Svendsen and K. Backe-Hansen (Pharm. Inst., Oslo Univ.). *J. Pharm. Pharmacol.*, 1959, **11** (10), 639-640.—To avoid occasional low results in the method of Svendsen and Aarnes (*Sci. Pharm.*, 1955, **23**, 18), as modified by Garratt *et al.* (*Anal. Abstr.*, 1958, **5**, 2754), extract the morphine from the  $\text{CHCl}_3$ -isopropyl alcohol soln. with 0.1 N NaOH (15 + 10 + 10 ml) and rinse the separator each time with  $\text{H}_2\text{O}$  (5 ml); add citric acid (0.5 g) to the combined aq. soln. and precipitate the morphine by addition of 1% 1-fluoro-2:4-dinitrobenzene soln. (50 ml). The recovery of morphine is probably  $\approx 95\%$ ; the coeff. of variation, estimated from 11 replicate determinations, is  $\approx \pm 1.45\%$ .

A. R. ROGERS

**2920. Coulometric determination of Dionin (ethylmorphine hydrochloride) and codeine phosphate.** K. Kalinowski and Z. Zwierzchowski (Zaklad. Chem. Farm., Akad. Med., Łódź). *Acta Polon. Pharm.*, 1959, **16** (5), 377-379.—A quant. micro-determination of codeine phosphate and ethylmorphine hydrochloride in an apparatus previously described (Kalinowski *et al.*, *Ibid.*, 1957, **14**, 77) has been carried out. The method involves bromination in an aq. medium with a slight excess of electrolytically generated bromine. Polarised platinum electrodes are used as an indicating circuit. *Procedure*—The aq. soln. of the substance (10 ml containing 2 to 5 mg) was introduced into the anode compartment, followed by 10 ml of 10% KBr soln. and 2 ml of 15%  $\text{H}_2\text{SO}_4$  soln. The cathode compartment (separated from the anode compartment by an asbestos diaphragm) contained 5% KBr soln. acidified with  $\text{H}_2\text{SO}_4$ . The indicating circuit was switched on, the soln. mixed by mechanical stirring and with the millivoltmeter needle set to zero, the generating circuit was switched on and the time ( $\pm 0.2$  sec.) was recorded when the needle was displaced from zero. A blank soln. was treated similarly. The accuracy was  $\approx \pm 1\%$ . The method requires  $\approx 10$  min. for a single determination.

W. ROUBO

**2921. Note on the use of citric acid and tartaric acid buffers in the extraction of solanaceous alkaloids by centrifugation.** D. P. N. Tsao (Coll. of Pharm., Univ. of Rhode Island, Kingston). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (9), 548.—The amounts of alkaloids extracted from belladonna and stramonium leaf are not significantly increased by the use of tartaric acid -  $\text{Na}_2\text{HPO}_4$  buffer instead of citrate buffer, or by the adoption of centrifugation instead of filtration for the removal of plant material from the extract. The use of the centrifuge is preferred in analysis because it reduces the time needed for separation from  $> 3$  hr. to about 20 min.

A. R. ROGERS

**2922. Microchemical identification of some atropine-like drugs.** E. G. C. Clarke (Dept. of Physiol., Royal Veterinary College, London). *J. Pharm. Pharmacol.*, 1959, **11** (10), 629-636.—Crystal and colour tests are described for 48 atropine-like drugs. The sensitivities are mostly  $< 1 \mu\text{g}$ . (*Cf. Anal. Abstr.*, 1955, **2**, 2201; 1958, **5**, 4303; 1959, **6**, 328.)

A. R. ROGERS

**2923. The determination of atropine and tropic acid.** J. Levine and J. E. Roe (Div. of Pharm. Chem., Food and Drug Administration, Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1959, **42** (4), 693-696.—Atropine and tropic acid may be separated from each other and from preservatives

such as benzyl alcohol or phenol by partition chromatography and determined by a modified Vitali procedure. The chromatographic procedure employs two columns connected in series, with Celite 545 as supporting phase. In column A the sample (2 ml), made alkaline with N NaHCO<sub>3</sub> (1 ml), adsorbed on Celite (4 g + 1 g), constitutes the stationary phase, and in column B the stationary phase is 0.2 N  $\text{H}_2\text{SO}_4$  (2 ml) adsorbed on Celite (3 g + 1 g). On washing the columns with  $\text{CHCl}_3$  (100 ml, + 25 ml through column B only), tropic acid remains on column A, atropine is adsorbed in column B, and preservatives pass both columns. Tropic acid is eluted from column A with ether after acidification of the column with acetic acid in ether, and atropine is eluted from column B with  $\text{CHCl}_3$  after neutralisation of the column with aq.  $\text{NH}_3$ . The alkaloid and tropic acid are converted into their salts by addition of HCl and aq.  $\text{NH}_3$ , respectively, and evaporated to dryness. For the modified colorimetric procedure, treat the dry residue on a steam bath for 30 min. with fuming  $\text{HNO}_3$  (1 ml) in a covered flask. Add water (10 ml), aq.  $\text{NH}_3$  (2 ml), sodium dithionite (about 50 mg) and 5%  $\text{NaNO}_2$  soln. (5 ml), and heat for a further 5 min. Cool and add conc. HCl (1 ml). After 5 min. add 5% sulphamic acid soln. (10 ml) and remove nitrous fumes in a current of air. Add 25 mg of solid N-1-naphthylethylenediamine dihydrochloride, make up to volume, set aside for 0.5 to 4 hr. and compare the extinction at 550 m $\mu$  with values obtained from standards treated similarly. Beer's law is obeyed up to at least 4 mg. Recoveries were from 100 to 103%.

E. C. APLING

**2924. Colorimetric determination of ephedrine hydrochloride and ephedrone hydrochloride.** Rhei Fujimoto and Shinsuke Ose (Dainippon Pharm. Co., Ltd., Fukushima-ku, Osaka). *J. Pharm. Soc. Japan*, 1959, **79** (3), 371-374.—The reaction of ephedrine (I) with ninhydrin yields a violet colour at pH 8.0, while that of ephedrone (II) yields a reddish-violet colour. At pH 5.0 the reaction of II with ninhydrin produces a reddish-brown ppt., while I remains colourless. *Procedure*—Soln. of a mixture of I and II (0.10 to 0.40 mg per ml) are treated with ninhydrin soln. at pH 5.0 and 8.0, then extracted with amyl alcohol, and the extinctions of the org. layers are measured. Calibration curves are given.

S. NATORI

**2925. Estimation of ergot alkaloids in cultures of *Claviceps purpurea*.** L. C. Vining and W. A. Taber (Nat. Res. Council of Canada, Prairie Reg. Lab., Saskatoon, Saskatchewan). *Canad. J. Microbiol.*, 1959, **5** (5), 441-451.—The method described is suitable for the routine assay of cultures and is preferred to methods which involve ion-exchange purification or fluorimetric determination. Recovery values range from 75 to 90%. The substances in the final test soln. that give a colour with the van Urk reagent (Alport and Cocking, *Yearb. Pharm.*, 1932, **5**, 341) consist entirely of ergot alkaloids, apart from occasional traces of tryptamine. *Procedure*—Freeze the culture (50 ml) at  $-40^\circ$  for 2 hr., add 10% aq.  $\text{NH}_3$  (1 ml) and diethyl ether (50 ml) and shake at room temp. for 30 min. Filter through sintered glass and wash the residue with ether ( $2 \times 10$  ml). Shake the combined ether soln. with 0.1 N  $\text{H}_2\text{SO}_4$  (3 ml or more). Add van Urk reagent (6 ml) to 3 ml of the separated aq. phase and measure the blue colour. The recovery is improved by four successive extractions of the sample with ether.

A. R. ROGERS

2926. Determination of harman, harmine and harmol in plant materials. J. Lutomski. *Biul. Inst. Rolin Leśniczych*, 1959, 5 (3-4), 169-182.—After the extraction of the alkaloids by the normal procedure the residue is dissolved in methanol and separated by paper chromatography with  $\text{CCl}_4$ -benzene-methanol (4:1:1). The spots are located with Amelink's modification of Dragendorff's reagent (*Pharm. Weekbl.*, 1931, 68, 159) and determined colorimetrically with Wasicky's *p*-dimethylaminobenzaldehyde reagent (*Z. anal. Chem.*, 1915, 54, 393). W. ROUBO

2927. Determination of epinephrine [adrenaline] in the presence of degradation products. Takeru Higuchi, T. D. Sokoloski and L. C. Schroeter (Sch. of Pharm., Univ. of Wisconsin, Madison, U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, 48 (10), 553-557.—The method of the U.S.P. XV (*cf. Welsh, Anal. Abstr.*, 1956, 3, 1483) is not reliable. The weighed product is usually not pure triacetyl-adrenaline and this leads to variable errors; the acetylation time should be limited to 2 or 3 min. Direct extraction of acetylation products may lead to recovery of acetylated forms of oxidised adrenaline, and a chromatographic step is preferred.

A. R. ROGERS

2928. Determination of adrenochrome monosemicarbazone. A. A. Patel and J. L. Patel (Almish Dept., Alembic Chemical Works Co. Ltd., Baroda, India). *Indian J. Pharm.*, 1959, 21 (9), 267.—Adrenochrome monosemicarbazone (I) in pharmaceutical preparations with sodium salicylate is determined by means of the colour developed on adding  $\text{Na}_2\text{CO}_3$  to a soln. of I containing HCl and  $\text{NaNO}_2$ . Procedure—A sample ( $\approx 10$  mg of I) is made up to 100 ml with water, a 10-ml aliquot is acidified, and free salicylic acid is extracted with diethyl ether. The aq. layer is made up to 100 ml, and to a 3-ml portion are added 2 ml of aq. HCl soln. (0.5%) and 2 ml of aq.  $\text{NaNO}_2$  soln. (0.5%). After 5 min. the yellow colour is discharged and 3 ml of aq.  $\text{Na}_2\text{CO}_3$  soln. (13.3%) is added. The soln. is made up to 12 ml and the extinction is measured at 430  $m\mu$  within 25 min. against a blank prepared similarly to the test soln. but omitting  $\text{Na}_2\text{CO}_3$ . A calibration curve is similarly prepared for the range 10 to 40  $\mu\text{g}$  from a standard soln. of I. The method gives a mean recovery of 99.6%  $\pm 0.52$ .

E. J. H. BIRCH

2929. Systematic chromatography of cardiac glycosides. A. Resplandy (Museum Nat. d'Histoire Naturelle, Paris, France). *Ann. Pharm. Franç.*, 1959, 17 (7-8-9), 536-543.—Cardiac glycosides can be chromatographed on paper with neutral aq. soln. of  $(\text{NH}_4)_2\text{SO}_4$  (up to 4 N) or aq. soln. of acetic acid (up to 20% by vol.). A rapid classification can be effected by simultaneous ascending chromatography for  $\approx 15$  min. with 2 N  $(\text{NH}_4)_2\text{SO}_4$  in one 250-ml flask and 8% acetic acid in another. Ouabain, K-strophanthin, convallatoxin, alostrophanthidin, tanghinoid, corchorin A, mansonin, cymar, strophanthidin, thevetin and thevetoside migrate with both soln., but bufotaline, protanghinin, oleandrin, scillaren A, nerifolin, digitoxigenin, monoacetylnerifolin, acetyl tanghinin and diacetylnerifolin migrate only with acetic acid. From these preliminary results a suitable soln. and concentration can be selected for longer chromatograms. The longer the sugar chain attached to the same genin, or the greater the number of free hydroxyl groups on the sugar, the greater is the  $R_F$  value. An

increase of hydroxyl groups on the genin also increases the  $R_F$  value. E. J. H. BIRCH

2930. Colorimetry of digitalis glycosides. Z. J. Vojdšek and B. Kakáč (Res. Inst. Pharm. and Biochem., Prague). *Českosl. Farm.*, 1959, 8 (10), 584-597.—A critical review, with 212 references. J. ZÝKA

2931. Occurrence, properties, structure, tests and chemical evaluation of anthracene derivatives in drugs. L. Kraus (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1959, 8 (9), 520-533.—A survey with 219 references. Volumetric, gravimetric, colorimetric, fluorimetric, polarographic, chromatographic and electrophoretic methods are reviewed. J. ZÝKA

2932. Chemical determination of the active principles of senna. T. Kartnig (Pharmakog. Inst., Univ., Graz, Austria). *Pharm. Zentralh.*, 1959, 98 (9), 495-499.—Procedure—Mix the powdered sample (100 mg) with acetic acid (8 ml) and conc. HCl (1 ml) and heat gently under reflux for 10 min. Add 30%  $\text{H}_2\text{O}_2$  soln. (0.1 ml) and heat for 5 min. Add diethyl ether (30 ml) and heat for 15 min. Filter through cotton wool and completely transfer the soluble material with two further 10-ml portions of ether. Wash the combined filtrates with  $\text{H}_2\text{O}$  (3  $\times$  30 ml), filter the ether layer and dilute it to 100 ml. Pass a 10-ml aliquot through successive columns of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  (3 g) plus kieselguhr (1 g) and of  $\text{NaHCO}_3$  (4 g). Wash the columns with ether (3  $\times$  5 ml). To determine the acidic sennosides, remove the ether from the  $\text{NaHCO}_3$  column *in vacuo*, dissolve the  $\text{NaHCO}_3$  in 20 ml of 4% aq. NaOH soln. containing 2% of 25% aq.  $\text{NH}_3$  soln., heat the soln. in boiling water for 4 min., cool and measure the extinction at 500  $m\mu$ . To determine the non-acidic emodins, shake the combined ether eluates with the aq.  $\text{NH}_3$ -NaOH soln. (20 ml) and measure colorimetrically as for sennosides. The results for 7 samples of senna leaf and 3 of fruit are in good agreement with those obtained by the method of Auterhoff (*Arzneimittel-Forsch.*, 1951, 1, 412). A. R. ROGERS

2933. The colorimetric determination of penicillin as the ferric hydroxamate complex. L. Mázor and M. K. Pápay (Inst. of Gen. Chem., Tech. Univ., Budapest, Hungary). *Z. anal. Chem.*, 1959, 171 (2), 98-103.—The test soln. containing 0.3 to 5.0 mg of penicillin is treated with 1 ml of hydroxyammonium chloride soln. ( $\approx M$ , adjusted to pH 6 with alkali) and 1 ml of  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  soln. ( $\approx M$ ) and a little acetic acid. The coloured complex is extracted by shaking with isobutyl alcohol and the organic phase is diluted to 10 ml with isobutyl alcohol. The absorption of this soln. is measured with the use of a blue filter (470 to 500  $m\mu$ ). The method is applicable to penicillin preparations and fermentation soln. H. M.

2934. Chemical method for the determination of antibiotics. VII. Colorimetric determination of oleandomycin. Tsuneko Miyake (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1959, 79 (1), 29-32.—The chemical determination of oleandomycin (I) was studied. An aq. soln. of I phosphate is warmed with diazotised sulphuric acid soln. in the presence of pyridine for 30 min. at 30°. The yellow soln. is treated with ethanol and aq. ascorbic acid soln. to give a pink colour. The extinction at 522  $m\mu$  is proportional



to the concn. of **I** over the range from 25 to 300  $\mu\text{g}$  per ml. The results agree well with those by bioassay. S. NATORI

**2935. Determination of a mixture of thiolutin and aureothricin by infra-red spectrophotometry.** Akira Ito and Osamu Amakasu (Takamine Res. Lab., Sankyo Co., Ltd., Shinagawa-ku, Tokyo). *J. Pharm. Soc. Japan*, 1959, **79** (2), 223-225.—The assay of a mixture of thiolutin and aureothricin was carried out by i.r. absorption spectroscopy, the bands used being at 973 and 943  $\text{cm}^{-1}$ , respectively (KBr disc). S. NATORI

**2936. Physico-chemical methods for the determination of antibiotics. IX. Photometric determination of polymyxin.** V. D. Kartseva and B. P. Bruns (All-Union Sci. Res. Inst. of Antibiotics, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 628-629.—Polymyxin (**I**) gives the biuret reaction with  $\text{CuSO}_4$  soln. in the presence of alkali, to produce a violet colour, the extinction of which is proportional to the concn. of **I**. To 10 ml of a soln. of **I** (500 to 1500  $\mu\text{g}$  per ml) add 10 ml of 0.5%  $\text{CuSO}_4$  soln. and 4 ml of 0.5 N NaOH; filter off the copper hydroxide, and measure the extinction of the clear filtrate; use a calibration curve to find the concn. of **I**. Glycine, histamine and NaCl have practically no influence on the extinction; methanol increases it. The method may be used to determine **I** in dry materials and in concentrates and eluates obtained by the desorption of **I** from cationites. C. D. KOPKIN

**2937. Spectrophotometric determination of psicofuranine. Elimination of monosaccharide interference in the determination of a nucleoside.** A. A. Forist (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1767-1768.—The antibiotic psicofuranine (**I**, cf. Eble *et al.*, *Anal. Abstr.*, 1960, **7**, 1896) in the presence of its hydrolysis product, psicose, is determined, after elimination of the psicose by reduction with sodium borohydride, by its reaction with diphenylamine. The resulting colour is measured at 630  $\text{m}\mu$ . The mean recovery and standard deviation of the method in the presence of 3.3 to 35% of psicose is  $100.4 \pm 2.0\%$ . G. P. COOK

**2938. Microchemical reactions of barbiturates with copper acetate and amines.** H. M. Romijn. *Pharm. Weekbl.*, 1959, **94** (18), 588-593.—Several combinations of Cu acetate, Co acetate and other acetates with a number of amines were tested for their ability to form well-defined coloured crystals with barbiturates. Only Cu acetate and Co acetate give coloured crystals; the turbidity of the latter reagent renders it unsuitable. Of the amines investigated, methylamine, ethylamine and ethylenediamine gave the best results. A mixture of 1 to 2 mg of the barbiturate and about the same amount of Cu acetate was transferred to one drop of the amine soln. and the crystals obtained were examined microscopically ( $\times 50$ ). The crystals given by 15 barbiturates with 3 mixtures are described and illustrated by 18 photographs. M. J. MAURICE

**2939. Separation of Novocain [procaine] from adrenaline in solution.** S. Bruno and E. Arbore (Ist. Chim. Farm., Univ. di Bari, Italy). *Boll. Soc. Ital. Biol. Sper.*, 1959, **35** (18), 1108-1111.—For therapeutic purposes, procaine is often used in soln. with adrenaline. Such soln. are subject to autoxidation, with resulting loss of physiological action and increased toxicity. The following method enables

procaine and adrenaline to be separated from each other and from their transformation products, and then determined. *Procedure*—Measured amounts of soln. were submitted to descending chromatography on Whatman No. 4 paper, in a solvent consisting of 95 ml of a mixture of *n*-butanol (400 ml) and 2 N acetic acid (115 ml), and 5 ml of ethanediol. The spots were revealed by treatment with iodine vapour, and the following  $R_f$  values were obtained—adrenaline, 0.25; procaine, 0.56; diethylaminoethanol, 0.40; and *p*-aminobenzoic acid, 0.82; oxidation products of adrenaline ran with the solvent front. For determination, the procaine spot was cut out, eluted with dil. HCl (1:10) and the colour developed after diazotisation and coupling with *N*-1-naphthylethylenediamine hydrochloride was measured at 545  $\text{m}\mu$ . The adrenaline spot was eluted with 0.01 N HCl, and the eluate was treated with 5% ammoniacal NaCN soln., followed by a soln. of arsenotungstophosphoric acid. The colour developed was read and reference was made to a standard curve to determine the adrenaline content. C. RAINBOW

**2940. Colorimetric determination of lidocaine [lignocaine] with *cis*-aconitic anhydride.** E. G. Feldmann and H. M. Koehler (Div. of Chem., American Dental Ass., Chicago, Ill.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1959, **48** (10), 549-552.—A method used by Sass *et al.* (*cf. Anal. Abstr.*, 1958, **5**, 3026) for the estimation of tertiary amines has been applied to the determination of lignocaine in small samples with a coeff. of variation of 1.1% (based on 8 replicates). *Procedure*—Make alkaline an aq. soln. of the sample by addition of aq.  $\text{NH}_3$  and extract at once with toluene. To a 2-ml aliquot of the centrifuged toluene soln. (containing 24 to 240  $\mu\text{g}$  of lignocaine) add 1 ml of reagent [dissolve *cis*-aconitic anhydride (250 mg) in acetic anhydride (40 ml), dilute to 100 ml with toluene and allow to age for 24 hr. before use] and heat in a bath of boiling water for 45 sec. Set aside for 15 min., dilute to 10 ml with acetic anhydride-toluene (1:4), mix, set aside for a further 15 min. and measure in a Klett-Summerson colorimeter with a No. 54 filter. Determine the reagent blank. Calculate by use of a standard curve.

A. R. ROGERS

**2941. Determination of methenamine [hexamine] and methenamine mandelate by nesslerisation following dilute acid hydrolysis.** B. W. Griffiths and J. E. Logan (Dept. of Nat. Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 1959, **31** (11), 1882-1884.—After hydrolysis with dil.  $\text{H}_2\text{SO}_4$  for about 25 min., to remove interfering formaldehyde from the soln., hexamine (**I**) and hexamine mandelate (**II**) can be determined colorimetrically, at 465  $\text{m}\mu$ , with Nessler reagent. Mean recoveries of 101.2 and 99.1%, and coeff. of variation of 1.09 and 0.73%, were obtained for the **I** and **II** determinations, respectively. The method was successfully applied to the determination of microgram amounts of **II** in bacterial sensitivity discs. G. P. COOK

**2942. Analytical review of current tuberculostatics with reference to the evaluation of some combined pharmaceutical preparations.** V. Spinková (State Inst. for Control of Drugs, Prague). *Českosl. Farm.*, 1959, **8** (9), 516-520.—The chemotherapeutic agents (derivatives of thiosemicarbazone, isoniazid, 4-aminosalicylic acid, pyrazinamide) and antibiotics (streptomycin, dihydrostreptomycin, cycloserin, neomycin and viomycin) and various

methods for their determination are reviewed and discussed. (49 references.) J. ZÝKA

**2943. Photometric determination of isonicotinic acid hydrazide [isoniazid], its derivatives and their metabolites in biological samples.** I. W. Nielsch and L. Giefer (J. A. Benckiser G.m.b.H., Ludwigshafen/Rhein). *Arzneimittel-Forsch.*, 1959, **9** (10), 636-641.—Isonicotinic acid (I) is decomposed with cyanogen chloride to a carboxyglutaconic dialdehyde which reacts with barbituric acid to give a blue polymethine dye. Isoniazid and its metabolites are first hydrolysed to I by alkali or extracted from biological samples with  $\text{CHCl}_3$ -benzoic acid and treated with  $\text{HNO}_2$ . The samples containing I are then treated with cyanogen chloride (prepared *in situ* from soln. of KCN and chloramine T) and barbituric acid and the extinctions are read. Procedures are given for the determination of I (extinction read at 600  $\mu$ ) and N-isonicotinoylglycine (extinction read at 615  $\mu$ ) in urine and plasma. Isoniazid and its metabolites on paper-chromatogram strips may be detected by treatment with gaseous cyanogen chloride and a barbituric acid spray reagent. This test will detect 0.01  $\mu$ g of I or 0.05  $\mu$ g of a derivative.

A. G. COOPER

**2944. Qualitative analysis of some sulphonamides by paper chromatography.** E. Sophoulis (Pharmacie Normale, Port Said, Egypt). *Ann. Pharm. Franç.*, 1959, **17** (6), 446-453.—The qualitative detection of sulphonamide drugs in pharmaceutical preparations is studied. *Procedure*—A sample containing 0.50 g of sulphonamides is shaken for 5 min. with 10 ml of a soln. made by making 10 ml of official aq.  $\text{NH}_3$  soln. and 40 ml of official acetone up to 100 ml with water. The mixture is centrifuged and the supernatant liquid is made up to 50 ml with water. Any residue is extracted with N HCl (to extract sulphaguanidine). The chromatography is effected by the ascending technique on Whatman No. 1 paper. Spots are revealed with a modified Ehrlich reagent (2 g of *p*-dimethylaminobenzaldehyde, 2 g of official HCl soln., and *n*-butanol to 100 ml). Solvent A [*n*-butanol (100 ml) - aq.  $\text{NH}_3$  soln. (28° Bé) (3 ml), satd. with water] separates sulphacetamide (I), sulphamerazine, sulphathiazole (II), sulphaguanidine (III) and sulphaniilamide (IV), but sulphamethazine (V) has the same  $R_F$  as II and sulphapyridine (VI) as III. Reduction of the alkalinity of solvent A (3 drops of aq.  $\text{NH}_3$  soln. instead of 3 ml) alters the  $R_F$  values and permits the separation of I and sulphadiazine (VII) and of II and V. Similar results are obtained, with rather higher  $R_F$  values, by adding methanol or ethanol to solvent A. The best separation of I, IV, V, VI and VII was achieved with *n*-butanol-methanol- $\text{CHCl}_3$ -2% aq.  $\text{NH}_3$  soln. (5:5:10:1) (solvent B). Unknown mixtures of the eight compounds can be separated by two-dimensional chromatography with solvents A and B.

E. J. H. BIRCH

**2945. Determination of sulphafurazole.** Toyozo Uno, Masao Kono, Tosiko Miyai and Hiroyuki Yasuda (Pharm. Inst., Med. Fac., Kyoto Univ., Sakyo-ku). *J. Pharm. Soc. Japan*, 1959, **79** (1), 113-115.—The general method of nitrous acid titration for sulpha drugs is not applicable to sulphafurazole (I). A new method for its determination was devised by converting I into acetylsulphafurazole. The sample of I ( $\approx$  500 mg) is dissolved in 0.7 ml of pyridine by warming, and treated with 0.2 g of acetic anhydride for 10 min. at 0° to 2°. The excess of acetic anhydride is decomposed with

water (1 ml), the ppt. is dissolved in acetone (25 ml) and the soln. is titrated with 0.1 M  $\text{NaNO}_2$  after the addition of 10% HCl soln. (20 ml) and water (10 ml); I can be accurately determined if the sample does not contain more than 5% of other sulpha drugs. S. NATORI

**2946. The estimation of N'-*p*-chlorophenyl-N'-isopropylidiguanide [proguanil] by use of a modified Sakaguchi reaction.** T. P. Owens and L. S. Malowan (Dept. Biochem., Univ. of Panama). *Arzneimittel-Forsch.*, 1959, **9** (10), 655-656 (in English).—*Procedure*—Add an aq. soln. (6 ml) containing 25 to 500  $\mu$ g of proguanil per ml to 8 drops of freshly prepared potassium hypobromite soln. (0.7 to 1 ml of bromine dissolved in 50 ml of 10% KOH soln.), add isopropyl alcohol (3 to 4 ml) and determine the transmission at 530  $\mu$ . The addition of 1-naphthol is unnecessary. A. G. COOPER

**2947. Estimation of halogen derivatives of 8-hydroxyquinoline.** K. G. Anantanarayanan, V. G. Kudalkar, M. S. Madiwale, H. H. Desai and M. B. Walawalkar (Dept. of Pharmacol., Haffkine Inst., Bombay, India). *Indian J. Pharm.*, 1959, **21** (9), 263-266.—Iodochlorhydroxyquinoline (I) and di-iodohydroxyquinoline (II) in pharmaceutical preparations are determined by the pptn. and weighing of the Cd complex. *Procedure*—The sample (containing  $\approx$  0.1 g of I or II) is dissolved in water and extracted with diethyl ether (5  $\times$  25 ml) or in some cases more satisfactorily with benzene; in one instance it was necessary to extract continuously with ether in a Soxhlet apparatus. After being washed with water and N HCl, the ether extract is evaporated, and the residue is dissolved in 20 to 40 ml of hot acetone. A 10% acetone soln. of  $\text{CdI}_2$  (2 ml) is added and then 2 g of anhyd. Na acetate. The addition of 5 volumes of water completes the pptn., and the washed ppt. is dried at 120° to 130°, and weighed. Results for the analyses of drug mixtures are compared with those by the N.F. X and U.S.P. XV methods. Chloroquine, some sulpha drugs, most B vitamins and tablet excipients do not interfere. E. J. H. BIRCH

**2948. Turbidimetric detection of decamethonium [compounds].** B. Giovannella, C. Manni and G. Moricca (Clin. Chirurgica, Univ. di Roma, Italy). *Experientia*, 1959, **15** (10), 393-394 (in English).—When Nessler reagent is added to a soln. containing decamethonium salts, a turbidity develops within a few minutes, which, when measured at 580  $\mu$ , bears a linear relation to the concn. of the drug in the range 2 to 20  $\mu$ g per ml. The reaction is specific for methonium salts when it is carried out in 2 M NaCl at a pH between 10 and 13. The method has been applied to the determination of decamethonium salts in biological fluids. P. NICHOLLS

**2949. Determination of Flaxedil [gallamine triethiodide].** P. Spacu and E. Antonescu (Centre Chem. Res., Acad. R.P.R., Bucharest, Romania). *Acad. R.P.R., Stud. Cercet. Chim.*, 1959, **7** (3), 389-397.—Methods are described for the gravimetric determination of gallamine triethiodide (I) with  $\text{K}_2[\text{Cr}(\text{SCN})_4] \cdot 4\text{H}_2\text{O}$  (II), the gravimetric and spectrophotometric determination with ammonium reineckate (III) and the potentiometric titration with  $\text{KBrO}_3$ -KBr soln. *Procedures*: (i) *determination with II*—The soln. of I is treated with 1 to 2 ml of HCl ( $d = 1.19$ ) and then with a conc. soln. of II until the supernatant liquid becomes violet. The mixture is well stirred, set aside for 5 min., and the

pptd. complex is filtered off in an  $A_2$  or  $A_3$  crucible, washed till free from  $Cl^-$  and dried at  $120^\circ$ . The factor is 0.9784, and results are accurate to  $\pm 0.15\%$ . (ii) **Determinations with III:** (a) *gravimetric*—The soln. of **I** is acidified with 0.5 to 1 ml of dil. acetic acid followed by a 1% soln. of **III** until the liquid becomes intensely red. The ppt. is coagulated by heating to  $70^\circ$ ; the mixture is then cooled in ice, and the ppt. is filtered off, washed with water till the washings are colourless, and dried at  $110^\circ$ . The factor is 0.6081. Results are accurate to  $\pm 0.2\%$ . The method can be used for micro-determinations. (b) *Spectrophotometric*—The ppt., obtained as described above, is dried on the filter *in vacuo*, and dissolved in acetone. The soln. is made up to 25 ml with acetone, and the extinction is read in a Pulfrich photometer with a yellow filter (max. absorption is at 533 m $\mu$ ). The accuracy is  $\pm 0.7\%$ . (iii) *Potentiometric titration*—The sample (0.03 to 0.05 g) is dissolved in 100 ml of water and treated with 5 ml of  $HCl$  ( $d = 1.19$ ). The soln. is then titrated with 0.1 N  $KBrO_3$ - $KBr$  at room temp., with a platinum-calomel electrode system. The complete oxidation of the iodine is indicated by a sharp rise in potential from the initial value of 180 to 206 mV. Near the end-point, 2 to 3 min. should be allowed for equilibrium to be reached. The accuracy is  $\pm 0.25\%$ . H. SHER

**2950. Determination of neostigmine in pharmaceutical preparations.** R. Biffoli (Lab. Chim. Provinciale, Firenze, Italy). *Boll. Lab. Chim. Provinciali*, 1959, 10 (4), 375-379.—Aqueous solutions of neostigmine exhibit an absorption maximum at 260 m $\mu$  and a minimum at 235.5 m $\mu$ . The absorption at 260 m $\mu$  obeys Beer's law over the range 50 to 1000  $\mu g$  per ml. E. C. APLING

**2951. Polarographic determination of derivatives of 5-nitrofuran. I. Determination of 5-nitro-2-furfuraldehyde semicarbazone in pharmaceutical preparations.** H. Marciszewski (Dept. of Anal. Chem., Inst. of Pharm., Warsaw). *Chem. Anal., Warsaw*, 1959, 4 (3), 577-581.—The dependence of the half-wave potential on pH in the polarographic determination of 5-nitro-2-furfuraldehyde semicarbazone (**I**) has been studied in 10% propane-1:2-diol soln. buffered with Britton and Robinson's buffer. The best pH range for quant. determination is 5 to 6, and a calibration curve is given covering the range 0 to 50  $\mu g$  of **I** per ml. Under the polarographic conditions given, the accuracy claimed is 2% for pure **I** and 4% for **I** in preparations. W. B. MIASKOWSKI

**2952. Polarographic determination of 6-azauracil.** F. Icha (Penicilin n.p., Roztoky u Prahy, Czechoslovakia). *Ceskosl. Farm.*, 1959, 8 (7), 384-385.—6-Azauracil (**I**) yields a well-developed polarographic wave in a medium of pH 1.95 to 10, which corresponds to a two-electron reaction; the height decreases with increasing pH and the wave disappears at pH > 11. In Britton and Robinson's buffer soln. of pH 7 to 8 the height of the wave ( $E_h = -1.18$  V at pH 7.2) is directly proportional to the concn. of **I**. *Procedure*—Dry the sample ( $\approx 115$  mg) for 2 hr. at  $60^\circ$  *in vacuo*, dissolve in  $H_2O$  by warming and dilute to 100 ml. To 1 ml of the soln add buffer soln. (9 ml), remove  $O$  with a stream of  $N$  and register the wave from  $-0.6$  V. Compare with a standard. J. ZÝKA

**2953. Analytical study of NN'-bis-(N-methyl-quinolinylurea) methylsulphate [Acaprin (Bayer)]. I. Gravimetric and volumetric determination.** V.

Špinková and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Ceskosl. Farm.*, 1959, 8 (10), 551-556.—Various methods are recommended for the determination of NN'-bis-(N-methylquinolinylurea) methylsulphate (**I**) and its injection soln. In one, the sample (100 mg) is dissolved in  $H_2O$  (10 ml), then boiled for 6 hr. under reflux with  $HCl$  (25%) (25 ml), cooled and titrated electrometrically (platinum-graphite electrodes) with 0.1 N  $NaNO_2$ . Another method is based on the gravimetric determination of the methylsulphate group of **I** as  $BaSO_4$  after hydrolysis with  $HCl$ . The reaction of **I** with picric acid can be used for the microscopical detection and for the gravimetric determination, and a similar gravimetric procedure is suggested with tungstosilicic acid as reagent. An indirect method is based on the pptn. of **I** with a known amount of  $K_2Cr_2O_7$  soln. and the iodimetric determination of the excess of the reagent. For a rapid testing of **I** the amperometric method with  $HgCl_2$  soln. as pptg. agent is recommended. *Procedure*—To about 100 mg of **I** add  $HCl$  (25%) (1 ml), dilute to 20 ml and titrate with 0.05 M  $HgCl_2$  (dropping mercury electrode - S.C.E.; 0 V). Measure the current density of the excess of the reagent. The reaction of **I** with  $HgCl_2$  soln. is also suitable for the microscopical identification of **I**. The most accurate results were obtained with the method based on the titration with  $NaNO_2$ . The errors of the methods described did not exceed  $\pm 1.5\%$ . J. ZÝKA

**2954. Contribution to the determination of pharmaceutically important organic nitrogenous bases by titration of their picrates in glacial acetic acid. I. Determination of some quaternary ammonium salts.** K. Howorka and M. Hádické (Staat. Inst. für Arzneimittelforschung, Jena). *Pharm. Zentralh.*, 1959, 98 (10), 538-545.—The method has been applied to the determination of benzylheptadecyldimethylammonium chloride (**I**), benzyltrimethylnonylammonium chloride, benzyl-dimethyloctadecylammonium chloride (**II**) and benzyl-dimethyltridecylammonium chloride (**III**) in the pure state or in simple preparations. *Procedure*—To the aq. soln. (5 ml containing 80 to 100 mg) add picric acid soln. of the D.A.B. VI (20 ml); with **I** or **III**, add also dil.  $HCl$  (1 ml). Heat on a bath of boiling water for 1 hr. (for 2.5 hr. with **I**), cool, filter through paper and wash the ppt. with picric acid soln. ( $3 \times 5$  ml). Transfer the ppt. to the original vessel with acetone, evaporate to dryness, dissolve the residue in glacial acetic acid (20 ml) and titrate with 0.1 N  $HClO_4$  in glacial acetic acid, with 0.1% crystal violet (2 drops) as indicator; with **II** use 0.1% crystal violet (1 drop) and 0.1% malachite green (3 to 6 drops) as indicator. A. R. ROGERS

**2955. Determination of mercury by distillation from its compounds and preparations.** H. E. Brookes and L. E. Solomon (Boots Pure Drug Co. Ltd., Pharm. Div., Standards Dept., Nottingham, England). *Analyst*, 1959, 84, 622-629.—The sample is distilled in a fused-silica flask, the distillate passes through a column of iron filings and  $CaO$  in the heated neck of the flask and the mercury is collected in a U-shaped receiver immersed in water and provided with a zinc-wool trap. The receiver is then placed in  $HNO_3$  and, when the zinc and mercury have dissolved, the soln. is oxidised with  $KMnO_4$  soln. and titrated with  $NH_4SCN$ , with  $(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3$  as indicator. With inorganic samples and preparations that are difficult to decompose, sucrose is added to the sample to provide



the flow of gas necessary to drive all the mercury into the receiver. The method is applicable to a wide variety of mercurial preparations, including tablets and pills, seed dressings and other mercury powders, and ointments.

A. O. JONES

**2956. Titrations with quinol and similar reducing agents. XV. Potentiometric micro-determination of gold in pharmaceutical preparations.** J. Doležal, M. Höfer and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1959, **8** (10), 557-561.—The potentiometric redoximetric determination of gold with quinol as volumetric reagent (Simon and Zýka, *Anal. Abstr.*, 1956, **3**, 2945) was used for the testing of preparations containing gold (in inorganic or organic combination), in the form of tablets, injections, emulsions, etc. In soln. of pH 2 to 7 as little as 1 µg of Au can be determined. The accuracy of the titration is not influenced by the presence of phosphates, nitrates or dilute aqua regia. Special procedures were developed for the decomposition of the various types of sample. The sodium salt of aurothiosuccinate and RbAuCl<sub>4</sub> (in a mixture with organic compounds) are decomposed with aqua regia, sodium aurothiosulphate by treatment with H<sub>2</sub>O<sub>2</sub> in an alkaline medium and then with aqua regia. Oil suspensions of aurothiolactobiose and aurothioglucose must be ignited and then dissolved in aqua regia. Thus, ignite the thoroughly mixed and shaken suspension (0.1 g) in a porcelain crucible, add aqua regia (1 ml), transfer to a porcelain dish and evaporate. Dissolve the residue in twice-distilled H<sub>2</sub>O, dilute to 100 ml, and to a 5-ml aliquot add H<sub>2</sub>O (10 ml), heat and titrate potentiometrically with 0.01 N quinol.

J. ZÝKA

**2957. Redoximetric determination of copper in some pharmaceutical preparations.** A. Berka and J. Zýka (Dept. Anal. Chem., Charles' Univ., Prague). *Českosl. Farm.*, 1959, **8** (10), 576-577.—**Procedure**—Dissolve the sample (about 10 mg of Cu) in H<sub>2</sub>O (35 ml), add Na acetate soln. (10%) (25 ml), NH<sub>4</sub>Cl (3 g) and NH<sub>4</sub>SCN soln. (10%) (10 ml), then dilute with H<sub>2</sub>O and titrate potentiometrically with 0.1 N quinol or slowly with 0.1 N hydrazine sulphate. To determine Cu in ointments, dissolve the sample in CHCl<sub>3</sub> (30 ml), add dil. H<sub>2</sub>SO<sub>4</sub> (1:1) (5 ml) and neutralise the soln. with NaOH soln. before the titration. **Indirect determination of reducing sugars, e.g., glucose**—To the sample (4 to 85 mg) add Fehling soln. I (10 ml) and II (10 ml), dilute with H<sub>2</sub>O to 50 ml, heat for 3 min. and boil for 2 min. (exactly). Cool, filter off and wash the ppt. with H<sub>2</sub>O, and dilute the filtrate to 100 ml. To a 25-ml aliquot add H<sub>2</sub>SO<sub>4</sub> (1:1) (0.6 ml), Na acetate (5 g), NH<sub>4</sub>Cl (6 g) and NH<sub>4</sub>SCN soln. (10%) (10 ml), dilute to 70 ml and titrate with 0.1 N quinol. Make a blank determination and determine the glucose content by reference to Schoorl tables.

J. ZÝKA

**2958. Radiometric analysis of some pharmacopoeial ointments and dusting powders. Determination of zinc.** J. Tölgyessy, M. Šaršunová and J. Majer (Dept. Radiochemistry, Tech. Univ., Bratislava, Czechoslovakia). *Českosl. Farm.*, 1959, **8** (10), 565-566.—The use of the radio-isotope <sup>65</sup>Zn enables a rapid radiometric determination of ZnO to be made, even when the volumetric method cannot be used. **Procedure**—To the sample (0.3 to 0.5 g) add dil. HCl (10 ml) and heat with occasional stirring until the soln. is clear. Add dil. H<sub>2</sub>SO<sub>4</sub> and hot H<sub>2</sub>O (20 ml) containing (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (5 g). Filter the hot mixture through a cotton plug, cool,

dilute to 50 ml and transfer 5 ml to a centrifuge tube. Add <sup>65</sup>ZnCl<sub>2</sub> soln. of such concn. that 0.2 ml of the mixture corresponds to 3000 to 5000 impulses per min. Transfer an aliquot (0.2 ml) to an aluminium dish, dry, and measure the activity. To the remaining soln. in the centrifuge tube add about two-thirds of the vol. of 0.025 N K<sub>2</sub>Fe(CN)<sub>6</sub>, required for the end-point. Centrifuge, and repeat the measurement of the activity with 0.2 ml of the supernatant liquid. An accuracy of ± 1% (— 2% for camphor-ichthammol ointment) was attained.

J. ZÝKA

**2959. Rapid method for the identification of metallic poisons.** G. Machata and H. Neuninger (Inst. f. Gerichtliche Med., Univ., Wien, Austria). *Arch. Toxikol.*, 1958, **17**, 41-47.—Dry tissue (20 g) or urine (100 to 200 ml, acidified with HNO<sub>3</sub> and evaporated to 20 ml) is heated under reflux for 3 to 5 hr. with conc. HNO<sub>3</sub> (50 ml) with gradual addition of 30% H<sub>2</sub>O<sub>2</sub> (10 to 20 ml). After cooling the liquid is filtered and the residue is washed with hot H<sub>2</sub>O. One half of the filtrate, together with the ashed residue, is evaporated to remove acid, dissolved in H<sub>2</sub>O to a known vol. (1 to 5 ml) and an aliquot (0.1 to 0.2 ml) of the well-mixed liquid is dried on a carbon or aluminium electrode and examined in a medium quartz spectrograph. The second half of the filtrate is examined for As by the Gutzeit test. A modification for the determination of As and Hg is described. The method has been successfully used for the identification of As, Au, Co, Cr, Hg, Mn, Sb, Si, Th, Tl and Zn.

S. BAAR

**2960. Radiometric determination of iodides and iodine in solutions of official ethanolic iodine-iodide solutions.** M. Šaršunová, J. Majer and J. Tölgyessy (Reg. Control Lab., Bratislava, Czechoslovakia). *Českosl. Farm.*, 1959, **8** (10), 567-568.—The method enables both components to be determined simultaneously with one volumetric reagent. **Procedure**—Dilute the sample (2 g) to 10 ml with ethanol (60%) (for ethanolic soln.) or H<sub>2</sub>O (for aq. soln.) and measure 2 ml into each of four test-tubes. To two test-tubes add different vol. of 0.1 N <sup>124</sup>Tl<sub>2</sub>SO<sub>4</sub> (more than required for the end-point in titrating I<sup>-</sup>) and to the other two test-tubes add 0.5 N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (0.5 ml) and a different vol. of 0.1 N <sup>124</sup>Tl<sub>2</sub>SO<sub>4</sub> (more than required for the end-point in titrating the total I<sup>-</sup> present in the sample as well as that formed by the reduction of free iodine). Dilute the contents of each test-tube with H<sub>2</sub>O to 10 ml, separate the ppt. by centrifuging, dry an aliquot of the supernatant liquid (0.2 ml) in an aluminium dish and measure the activity.

J. ZÝKA

**2961. Determination of the alcohol content of galenical preparations by observation of the boiling temperature.** H. Böhme and H. Hocke (Pharm.-Chem. Inst., Univ. Marburg, Lahn). *Dtsch. Apoth.-Ztg.*, 1959, **99** (39), 962-965.—A 2-ml sample of the spirit or tincture is heated under reflux (apparatus described and illustrated), and the b.p. (corr.) is determined from the equation b.p. (corr.) = b.p. (obs.) + 0.036(760 - p), where p is the atm. pressure (torr). A graph shows the variation of b.p. (corr.) with the concn. of alcohol [% (w/w)].

A. G. COOPER

See also Abstracts—2780, Determination of quaternary ammonium compounds. 2803, Diphenylamine in trichloroethylene. 2806, Identification of org. arsenic compounds. 2815, Determination

of piperazine. 2840, Determination of camphene. 2841, Determination of carvone. 2908, Chromatography of triamcinolone.

### Food

*Foods and food additives, beverages, edible oils and fats, vitamins.*

2962. Proximate analysis of wheat-flour carbohydrates. IV. Analysis of wholemeal flour and some of its fractions. J. R. Fraser and D. C. Holmes (D.S.I.R., Lab. of the Gov. Chemist, London). *J. Sci. Food Agric.*, 1959, 10 (9), 506-512.—Methods previously described for starch, pentosans or hemicelluloses, sugars and cellulose (Fraser *et al.*, *Ibid.*, 1958, 7, 577; Fraser and Holmes, *Ibid.*, 1956, 7, 589; 1957, 8, 715) are examined for their applicability to non-endosperm fractions containing large amounts of husk or fat, e.g., bran and germ. Minor changes in procedure, combined with certain modifications in the factors, yield satisfactory results for the "carbohydrate by difference" of all fractions of the wheat grain.

P. D. PARR-RICHARD

2963. Potentiometric titration of sulphhydryl [mercapto] groups in wheat gluten with iodine. W. C. Shaefer, C. A. Wilham, R. J. Dimler and F. R. Senti (Northern Reg. Res. Lab., Peoria, Ill., U.S.A.). *Cereal Chem.*, 1959, 36 (5), 431-441.—In order to avoid solubility and turbidity problems encountered in gluten mercapto-group analysis by the direct iodimetric method, titrations were made with a saturated solution of iodine in 0.01 N acetic acid (N atmosphere) recording the e.m.f. to the nearest mV 3 min. after each iodine addition. Tests with glutathione and 2-mercaptoethanol gave results in good agreement with theoretical, giving a standard deviation of 5.4% of the average titre. Proteins gave high results compared with other methods. Glutens reduced 6.4 to 9.8  $\mu$ equiv. of iodine per g of protein. No correlation appeared to exist between gluten reducing power and baking quality.

P. M. KINGSTON

2964. Determination of acidity in raw materials for dough and in dough products. A. Menger (Bundesforschungsanst. f. Getreideverarbeitung, Detmold, Germany). *Getreide u. Mehl*, 1959, 9 (4), 37-40.—The literature is reviewed, covering the fundamental chemistry of acid determination in cereal products, special problems connected with dough products and the development of a suitable method depending on alcohol extraction. The value of the Kreis-Arragon method is discussed and comparative data of that and three other methods, viz, extraction with 50% v/v ethanol; 67% v/v ethanol; and 67% v/v ethanol, according to "Schulerud" (*Cereal Chem.*, 1932, 9, 128) are given. In control tests, samples of finely milled Durum of particle size  $> 460 \mu$  and of powdered dough products of  $> 300 \mu$  were used with an extraction time of 1 hr. The official Italian method is recommended. The sample (4 g) is extracted with 50% v/v ethanol (100 ml). After 3 hr. it is filtered and aliquot portions of the filtrate are titrated with 0.02 N NaOH, to phenolphthalein. (14 references.)

S.C.I. ABSTR.

2965. Methods and problems of carotene analysis. S. Allavena (Lab. Provinc. di Igiene e Profilassi, Mailand). *Getreide u. Mehl*, 1959, 9 (4), 41-47.—This report is especially concerned with the determination of colouring matter and carotenoids in

flour, semolina and dough products, and the literature is reviewed. (26 references.)

S.C.I. ABSTR.

2966. Quantitative and qualitative determination of connective-tissue content of meat and meat products. F. Lörincz and I. Szeredy (Hungarian Meat Res. Inst., Budapest). *J. Sci. Food Agric.*, 1959, 10 (9), 468-471.—Connective tissue is determined from the difference between total N and the N extracted with alkali. *Procedure*—Chop the material in a standard manner and determine total N on 2 to 2.5 g. Weigh another 1-g sample into a 100-ml tube, add 0.05 N alkali (50 ml) and dilute to volume with  $H_2O$ . Keep at room temp. for 1 hr., shaking frequently, then filter. Determine N on 50 ml of the filtrate. Obtain connective-tissue N by difference. To separate collagen and elastin, wash the residue free from alkali and boil (with the filter-paper) for 1 hr. in 30 ml of  $H_2O$ . Add 0.2 g of tartaric acid, boil again for 30 min., make up to a known volume and filter. The filtrate contains the collagen N and the residue the elastin N. Results for meats from animals of different kinds and ages are compared.

P. D. PARR-RICHARD

2967. Methods for the chemical analysis of milk. British Standards Institution (2 Park St., London, W.1). B.S. 1741:1951. Amendment No. 1, 11.12.59.—The specification for test-tubes is changed.

2968. Applications and limitations of quality tests for milk and milk products. A review. C. K. Johns (Dept. Agric., Ottawa, Canada). *J. Dairy Sci.*, 1959, 42 (10), 1625-1650.—Bacteriological aspects are discussed and 176 references are given.

W. H. C. SHAW

2969. Determination of fat in mayonnaise. W. Diemair and M. Salvisberg (Univ. Inst. f. Lebensmittelchem., Frankfurt a. Main, Germany). *Z. Lebensmitteluntersuch.*, 1959, 110 (5), 366-371.—The results of seven standard methods are compared. Preference is given to the Hadorn and Jungkuntz method (cf. *Z. Lebensmitteluntersuch.*, 1951, 93, 277) with benzene-ethanol (1:1) as extracting solvent. The method shows a standard deviation of  $\pm 0.0170\%$  (for 6 results), and ensures practically complete extraction of the lecithin with the fat.

P. S. ARUP

2970. Methods for the analysis of water-soluble coal-tar dyes permitted for use in foods. British Standards Institution (2 Park St., London, W.1). B.S. 3210:1960, 34 pp.—Methods are specified for matter volatile at 135°, matter insol. in water, matter extracted by diisopropyl ether, determination of dye content, subsidiary dyes, chloride, sulphate, copper, arsenic and lead.

N. E.

2971. New method for the extraction and identification of synthetic colours in sugar-containing foods. F. M. Del Bianco and G. Trabacchi (Lab. Chim. della Camera di Commercio, Roma). *Chim. e Ind.*, 1959, 41 (9), 896-898.—A new rapid procedure is described for the identification of colours permitted by the new Italian laws in sugar-containing foods (jams, syrups, candies, etc.). It is based on selective extraction at different pH values, followed by identification by paper chromatography. Some typical analyses are described.

C. A. FINCH

2972. Artificial food colours. IV. Spectrophotometry of the green, blue and violet water-soluble colours in acid, neutral and alkaline media. A. Carballido and L. Villanúa (Dept. Invest. Bromatológicas, Univ. Madrid). *An. Bromatología*, 1959, 11 (3), 265-278.—Absorption maxima and curves in acid, neutral and alkaline soln. are reported graphically and in tabular form for the ten blue, green and violet colours permitted by Spanish legislation for use in food products. The colours dealt with include indigo carmine, methyl violet, Acid violet 6B (C.I. Acid Violet 17), Acid Violet 5BN (C.I. Acid Violet 24) and Brilliant green cryst. Y.

Appendix to Parts II, III and IV. A. Carballido and L. Villanúa. *Ibid.*, 1959, 11 (3), 279-285.—Spectrophotometric data for certain colours dealt with in earlier papers (cf. *Anal. Abstr.*, 1959, 6, 4966; and Part IV, above) are re-presented, classified according to the colour of their soln. in acid or alkaline media.

V. Circular paper chromatography of permitted water-soluble colours. M. T. Valdehita, R. García Olmedo and L. Villanúa. *Ibid.*, 1959, 11 (3), 287-300.—Chromatographic data are presented for the Spanish permitted water-soluble food colours. Chromatography was conducted on 12-cm S. & S. No. 2043a papers by the Rutter technique (*Analyst*, 1950, 75, 37), with development in a desiccator employed as a chamber saturated with the vapour of the developing solvent. Developing solvents were (i) *n*-butanol-ethanol-water (2:1:1) and (ii) solvent (i) plus 10% of aq.  $\text{NH}_3$  (0.924).  $R_F$  values and the appearance of the bands in ordinary and ultra-violet light are tabulated. Similar results were obtained with Whatman No. 1 paper.

E. C. APLING

2973. Chromatographic determination of polyoxyethylene glycol esters in bread and cakes. A. Boari (Lab. Chim. Prov. Bologna, Italy). *Boll. Lab. Chim. Provinciali*, 1959, 10 (3), 221-233.—Procedure.—The sample (10 g) of dried and ground bread (only the crumb) is heated with 25 ml of 6*N* HCl on a water bath for 10 min. Solid KOH (8 g) is added to the cooled product and the mixture is then reheated on a water bath for 30 min. The cooled liquid is adjusted to pH 3.7 with HCl (1:1), and after being filtered is extracted with  $\text{CHCl}_3$  ( $2 \times 25$  ml). The  $\text{CHCl}_3$  phase is evaporated and the residue is dissolved in 2 ml of 95% ethanol. A little of this soln. (6 or 8 drops) is applied to Whatman No. 1 paper [previously washed with  $\text{H}_2\text{O}$  and saturated with the developing solvent (*n*-butanol-acetic acid- $\text{H}_2\text{O}$ ) (4:1:5)], and developed by the ascending technique for 2 hr. The paper is dried and sprayed with modified Dragendorff reagent. A carmine-red spot ( $R_F$  between 0.64 and 0.66) indicates the presence of polyoxyethylene glycol esters.

L. ZANONI

2974. Detection and semi-quantitative estimation of chlorinated organic pesticide residues in foods by paper chromatography. P. A. Mills (Div. of Food, Food and Drug Admin., Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1959, 42 (4), 734-740.—Suitable extraction procedures are detailed for pesticide residues in large fruits; small soft fruits, vegetables, beans and dry feeds; fats and oils; cheese; milk; and animal tissues. Purification of the extracts by means of methyl cyanide-hydrocarbon partition and by means of columns of Florisil, magnesium oxide-Celite and sulphuric acid-Celite is described. For the paper chromatography on

Whatman No. 1 paper, suitable solvent systems are (i) *aqueous*: immobile solvent, liquid paraffin U.S.P. (or maize, cottonseed, tung or soya oil), 5% in ether; mobile solvent, 75% aq. acetone, 2-methoxyethanol or methanol, or 40% aq. pyridine, and (ii) *non-aqueous*: immobile solvent, dimethylformamide, 2-phenoxyethanol or dimethylcyanamide, 35% in ether; mobile solvent, 2:2:4-trimethylpentane or mixed octanes. For location of spots and semi-quant. estimation, the dried papers are sprayed with a reagent containing  $\text{AgNO}_3$  (1.7 g), water (5 ml), 2-phenoxyethanol (10 ml) and 30%  $\text{H}_2\text{O}_2$  (1 drop), diluted to 100 ml with acetone. The sprayed papers are then exposed to u.v. light until the reduced silver spots are developed. Recovery data are reported for 13 pesticides, and vary from 40 to 100%.

E. C. APLING

2975. Improved method for the determination of uric acid in insect-infested foodstuffs. S. Venkat Rao, K. Krishnamurthy, M. Swaminathan and V. Subrahmanyam (Central Food Technol. Res. Inst., Mysore, India). *Ann. Biochem.*, 1959, 19 (8), 187-190.—By determining the "uric acid" content of wheat flour (75% extraction), jowar, field bean and black gram with Benedict's reagent before and after treatment with uricase, 90 to 105% recovery of the "true" uric acid can be achieved. The method (which is specific for uric acid and indicates the degree of infestation) consists in aq. extraction at room temp. followed by removal of protein from the extract with tungstic acid and colorimetric determination of "total" uric acid by the method of Benedict and Franke (*J. Biol. Chem.*, 1922, 52, 387); a second portion of the extract (containing  $> 500 \mu\text{g}$  of uric acid) is treated with 10% of its vol. of 2% uricase soln. in borate buffer (pH 9.2) at 40° to 45° for 1 hr.; the "apparent" uric acid is then determined as before. Results for the uric acid content of foodstuffs infested with *Tribolium castaneum* H. under controlled conditions compared well with paper-chromatographic results for quantities down to 1 mg per 100 g.

P. M. KINGSTON

2976. Determination of inulin in chicory root. W. Wöhlert and U. Freimuth (Inst. f. Lebensmittel- u. Gärungschem., Tech. Hochschule, Dresden, Germany). *Z. Lebensmitteluntersuch.*, 1959, 110 (5), 371-375.—Current methods are criticised. The inulin contained in an aq. extract of the root is purified by a paper-chromatographic procedure in which a butanol-pyridine-water (6:4:3) mixture is used as ascending solvent. All the accompanying substances migrate, while inulin remains at or near the starting point. The time required for development may be 1 to 5 days according to the proportion of slowly-moving higher inulides in the sample. The inulin is determined colorimetrically by the anthrone- $\text{H}_2\text{SO}_4$  reaction (Dreywood's modification) (cf. *Ind. Eng. Chem., Anal. Ed.*, 1946, 18, 499) in an eluate of a square of the chromatographic paper including the starting point. The mean error on the mean of 20 determinations is  $\pm 0.1\%$ .

P. S. ARUP

2977. Determination of saffrole and methyl salicylate in soft drinks. J. B. Wilson (Div. of Food, Food and Drug Admin., Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1959, 42 (4), 696-698.—Saffrole and methyl salicylate are separated from the soft drink by steam-distillation, the distillate is saponified and saffrole is extracted with  $\text{CHCl}_3$ . Saffrole is determined spectrophotometrically, comparing the extinctions at 287  $m\mu$  and 308  $m\mu$  with



values obtained from prepared standards. For the determination of methyl salicylate, the extracted aq. soln. is evaporated to dryness and the salicylic acid in the residue is determined colorimetrically after the addition of ferric chloride and acetic acid. The extinction at 530 m $\mu$  is evaluated by comparing with values obtained from standards prepared by saponification of known amounts of methyl salicylate. Recoveries of safrole were from 96 to 104% over the range from 4 to 50 p.p.m. Recoveries of methyl salicylate were 85% or better for quantities up to 100 p.p.m. Results obtained for commercial root beers were from 10 to 20 p.p.m. of safrole and from 18 to 50 p.p.m. of methyl salicylate.

E. C. APLING

**2978. Determination of lemon juice in drinks and syrups.** C. Sampietro and I. Invernizzi (Lab. Chim. Prov., Como, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (3), 242-247.—It is pointed out that the determination of the formaldehyde number (which serves to establish the amount of fruit juice contained in a drink) is affected by the presence of SO<sub>2</sub>, which lowers this value.

L. ZANONI

**2979. Gas-chromatographic investigation of alcoholic beverages.** R. Mecke and M. de Vries (Inst. f. Phys. Chem., Freiburg i. Br.). *Z. anal. Chem.*, 1959, **170** (1), 326-332.—A procedure is described for the separation and identification of the aroma-producing compounds in wines and spirits. These are extracted from 300 ml of the sample with a mixture of diethyl ether and *n*-pentane (2:1). Traces of ethanol are removed by washing with water and the extract is dried over Na<sub>2</sub>SO<sub>4</sub>. The extractant is distilled off at 32° to leave a yellow oil (0.2 ml). This is analysed by vapour-phase chromatography. The identity of the components can be confirmed by running a series of chromatograms with the successive removal of the esters, aldehydes and alcohols as non-volatile derivatives. The procedure has been used to study the distillation of brandy, and may be suitable for quality control.

G. BURGER

**2980. Evaluation of the diastatic activity of brewing malts.** L. Weith. *Braueri, Wiss. Beil.*, 1959, **12** (10), 166-170.—Present-day knowledge of the formation of amylases during germination and its significance in the mashing process is summarised, and it is concluded that the  $\alpha$ -amylase formed during malting is the governing factor for the diastatic quality of brewing malts. Methods for determining diastatic activity by the Windisch-Kolbach and other procedures are discussed and criticised.

S. M. MARSH

**2981. Correlations between malt analytical data and brewing factors.** E. G. Martin and M. R. Sfat (Rahr Malting Co., Manitowoc, Wis.). *Proc. Amer. Soc. Brew. Chem.*, 1959, 10-17.—The results are presented of a study of the relationships between malt analysis data, brewhouse performance (run-off rate, extract yield and extraction efficiency) and analytical data for wort and beer (wort and beer protein and colour, real degree of fermentation, beer pH and colloidal instability); 21 graphs are given and correlation coeff. are calculated and discussed.

R. E. E.

**2982. Study of lead precipitation and spectrophotometric methods of hop analysis.** L. S. Gimbel, III, B. W. Schwartz and J. L. Owades (Schwartz Labs., Inc., Mt. Vernon, N. York). *Proc. Amer. Soc. Brew. Chem.*, 1959, 32-40.—The ASBC gravimetric

lead method ("Methods of Analysis. Hops," 1950, p. 133) is compared with a modification of the spectrophotometric method of Alderton *et al.* (*Anal. Abstr.*, 1954, **1**, 3138). For the latter, the sample (25 g) is ground and an aliquot (5 g) is shaken for 30 min. with toluene or light petroleum (100 ml). An aliquot (5 ml) of the clear supernatant liquid is diluted to 50 ml with freshly prepared alkaline methanol (2 ml of 6 N NaOH made up to 1 litre with anhyd. methanol). An aliquot (4 ml) of this soln. is then diluted to 100 ml with alkaline methanol, and the extinctions are read at 355, 325 and 275 m $\mu$ . The concn. of  $\alpha$ -acids and  $\beta$ -acids are calculated by the formulae previously given (*loc. cit.*) and divided by 2 to give percentages. Results by both methods on 91 samples of hops, both old and fresh, and covering 6 varieties, show good agreement for  $\alpha$ -acids, the spectrophotometric results being slightly higher. A comparison of the spectrophotometric results for  $\beta$ -acids with the gravimetric ones for the " $\beta$ -fraction" (which, besides lupulones, contains also "uncharacterised soft resins") shows that the value for the  $\beta$ -fraction can be obtained from the value for the  $\beta$ -acids by applying a variational factor (*i.e.*, 2.0 for Clusters, 3.7 for Fuggles and 3.4 for Bullions). A comparison of the spectrophotometric results for 199 hop samples, with toluene and light petroleum as solvents, disclosed no significant differences for  $\beta$ -acids, or for  $\alpha$ -acids in hops up to 3 months old; for older hops, however, toluene yielded significantly higher results for  $\alpha$ -acids, and should therefore be used for such hops, or for hops the age of which is uncertain.

R. E. E.

**2983. Evaluation of hops. VIII. Note on the preparation of extracts in the estimation of  $\alpha$ -acids.** J. R. Hudson (Brewing Ind. Res. Foundation, Nutfield, Surrey). *J. Inst. Brewing*, 1959, **65** (5), 422-423.—Hops (15 g) are shaken with toluene (100 ml) and about 12 ceramic balls (diam.  $\approx$  2.5 cm, wt.  $\approx$  16 g) in an atmosphere of N in a cylindrical tin for  $<$  3 min. The contents are decanted through glass wool and an aliquot is used for the usual titration.

N. E.

**2984. Chlorides in beer by ion exchange.** D. B. West and A. F. Lautenbach (J. E. Siebel Sons' Co., Inc., Chicago, Ill.). *Proc. Amer. Soc. Brew. Chem.*, 1959, 87-92.—*Procedure*—Prepare a column (12 in.) of Amberlite IR-120 (H form) and pass 6% HNO<sub>3</sub> soln. (50 ml) through at a rate of 1 drop per sec. Follow with 50 ml of water, back-wash with 250 ml of water, and bring the water level to 0.5 in. above the resin bed. Then pass 20 ml of de-gassed beer through at a rate of 1 drop per sec., rejecting the first 10 ml of percolate, which is water. When the beer has fallen to 0.5 in. above the resin bed, maintain this level by the addition of water, and collect 75 ml of percolate. To this add 10 drops of mixed indicator soln. (0.5% of diphenylcarbazone and 0.05% of bromophenol blue in 95% ethanol), and add 0.5 N NaOH till the soln. turns blue, then 0.2 N HNO<sub>3</sub> till the soln. turns yellow and 0.5 ml in excess. Then titrate with 0.025 N Hg(NO<sub>3</sub>)<sub>2</sub> to a blue-violet end-point. Recoveries of Cl<sup>-</sup> (92 to 368 p.p.m.) added to beer were 97.3 to 102.2%, with a range of 5 p.p.m. between duplicates. The results agreed well with those by the polarographic method of Strodts and Polky (*Ibid.*, 1953, 79) and that of Hansen and Molgaard (*Brygmesteren*, 1958, 15, 299), but the official AOAC ashing method ("Methods of Analysis," 8th Ed., 1955, p. 149) gave markedly lower results.

R. E. E.

**2985. Statistical control of alcohol and extract analyses in beer.** A. J. Byer (Wallerstein Labs, Staten Is., N.Y.). *Proc. Amer. Soc. Brew. Chem.*, 1959, 41-55.—Tabarié's principle [*Ann. Chim. (Phys.)*, 1830, 45 (Sér. 2), 222] expresses the relationship between sp. gr. of de-gassed beer ( $G$ ), of de-alcoholised beer ( $S_1$ ) and of the alcoholic distillate ( $A$ ) by the equations  $S_1 - G = 1 - A$ , or  $S_1 = 1 - A + G$ . In practice it is found that close agreement with the results of actual beer analysis is obtained only when the procedure is conducted on a gravimetric basis (i.e., 100 g of beer distilled, and distillate and residue made up to 100 g). In general, the Tabarié values ( $S_1$ ) for the sp. gr. of de-alcoholised beer are slightly higher than the observed values ( $S_w$ ), and when the sp. gr. are determined to the 5th decimal place the difference ( $X$ ) can be expressed as a whole number by the equations  $X = (1 - A + G - S_w) \times 10^5$ , or  $X = (S_1 - S_w) \times 10^5$ . Six nomograms, with the appropriate equations, are given, that express the interrelations between real extract, apparent extract, original extract, and percentages of alcohol by wt. and by vol.

R. E. E.

**2986. Adaptation of the immersion refractometer to the determination of extract and alcohol in the brewery.** L. S. Gamer (Olympia Brewing Co., Olympia, Washington, D.C.). *Proc. Amer. Soc. Brew. Chem.*, 1959, 102-106.—The results obtained from various published formulae for one light and one heavy beer are compared with those by the ASBC distillation method.

R. E. E.

**2987. Expanded nomograph technique applied to routine refractometric analysis of wort and beer.** J. E. A. Van Gheluwe, A. L. Stock and J. P. McRae (Molson's Brewery, Ltd., Montreal, Que., Canada). *Proc. Amer. Soc. Brew. Chem.*, 1959, 107-112.—Soluble extract in wort, and real extract and alcohol in beer, can be determined by a refractometric reading alone, or a refractometric reading and a sp. gr. determination, respectively. Formulae are given, modified from those of Geys (*Z. ges. Brauw.*, 1921, 44, 106) for wort and of Schild and Irrgang (*Brauwissenschaft*, 1957, 9, 314; 10, 19) for beer, from which nomograms can be constructed by ASBC methods ("Methods of Analysis. Beer," Chicago, 1956, p. 17).

R. E. E.

**2988. Electronic measurement of the oxygen dissolved in beer.** K. Silbereisen and C. Weymar (Versuchs- u. Lehranstalt f. Brauerei, Berlin). *Braueri, Wiss. Beil.*, 1959, 12 (10), 155-161.—Various methods for the determination of oxygen in beer are discussed. The use of electrochemical methods is then detailed. Modified Tödt apparatus (*cf. Ibid.*, 1952, 87) is used and various electrode combinations and types of electrode have been tested. The method is compared with colorimetric and volumetric procedures and found to be advantageous for accurate quantitative work. The use of the technique industrially is discussed and an apparatus for the continuous determination of oxygen in beer is described. Conditions required are temp. control, constant stirring, regular replacement of electrodes and exact calibration.

S. M. MARSH

**2989. Determination of carbon dioxide in wines by using a vacuum system.** M. J. Pro, A. Etienne and F. Feeny (Alcohol and Tobacco Tax Division Laboratory, Washington, D.C.). *J. Ass. Off. Agric. Chem.*, 1959, 42 (4), 679-683.—The method depends on measurement of the change of pressure

produced when the alkaline sample is acidified with phosphoric acid *in vacuo* in a specially designed all-glass apparatus (described). Interference by sulphur dioxide is eliminated by addition of  $H_2O_2$  to the acidified system. Correction factors for the effect of phosphoric acid on the vapour pressure of various wines are tabulated. Collaborative tests showed excellent agreement in the determination of carbon dioxide concentrations varying from 150 to 400 mg per 100 ml.

E. C. APLING

**2990. Determination of bromoacetic acid in wine.** B. Romani and I. Bastianutti (Lab. Chim. Prov. Udine, Italy). *Boll. Lab. Chim. Provinciali*, 1959, 10 (3), 216-220.—A 200-ml Kempf extractor is used to separate the bromoacetic acid, with diethyl ether as solvent. The extract is treated with 0.1 N  $KMnO_4$  in the presence of 2 N  $H_2SO_4$  until a pale-pink colour persists for some minutes. The filtered liquid is extracted ( $\times 3$ ) with diethyl ether and the residue after evaporation is used for the chromatographic separation. The ascending technique and Whatman No. 1 paper are used with cyclohexane-dioxan-acetic acid- $H_2O$  (5:4:2:2) as developer. After saturation of the paper with  $NH_3$  and drying at 100° the chromatogram is treated with a mixture of phenol red and acetic acid in acetone soln. and chloramine-T soln. (0.25 g in 15 ml of  $H_2O$ ). Blue spots of  $R_f$  0.25 are obtained. The sensitivity is 10 mg per litre.

L. ZANONI

**2991. New direct volumetric determination of iodine value.** I. Napoli (Lab. Chim. Provinciale, Frosinone, Italy). *Boll. Lab. Chim. Provinciali*, 1959, 10 (4), 346-354.—An electrometric determination of iodine values with a 0.15 N solution of Br in glacial acetic acid, a simple transistor indicator circuit and a platinum double electrode is described. The method is simple, rapid and precise, but iodine values obtained are, in general, lower than by the methods of Hübl, Wijs and Hanus.

E. C. APLING

**2992. Determination of the degree of oxidation of olefinic fats.** K. Täufel and R. Zimmermann (Dtsch. Akad. Science, Inst. Nutr., Potsdam, Germany). *Fette, Seif., Anstrichmitt.*, 1959, 61 (10), 836-841.—Autooxidation of olefinic acids by u.v. light initially causes the formation of hydroperoxides. Their formation induces secondary reactions which lead to the formation of peroxides and a number of carbonyl compounds. The standard iodimetric method of determination of autooxidation gives only a measure of the hydroperoxides themselves. Three methods were applied in order to obtain a more accurate measure of the degree of autooxidation and the types of products formed. The determination of the "peroxide" number gives a measure of "active" oxygen. The benzidine method (*cf. Möller, Ibid.*, 1958, 60, 465) gives the total amount of carbonyl compounds present. The thiobarbituric acid method determines malonaldehyde. As such it is suitable for the determination of the autooxidation products of linoleic and linolenic acids. Technical details of the methods are given. As a result of autooxidation of some saturated and unsaturated acids, products are formed that show an absorption maximum corresponding to crotonaldehyde and acetaldehyde.

S. BAAR

**2993. The analysis of lipids by means of radioactive reagents.** H. K. Mangold (Hormel Inst., Univ. Minnesota, Austin, Minn., U.S.A.). *Fette, Seif., Anstrichmitt.*, 1959, 61 (10), 877-881.—Fatty acids can be methylated with [ $^{14}C$ ]diazomethane, while

acids containing hydroxyl groups or amino groups can be acetylated with  $^{14}\text{C}$ acetic anhydride. Lipids (5 to 10 mg) can be quant. analysed on a silicic acid column by elution with aq. acetic acid- $\text{CHCl}_3$ -methanol mixtures. Five fractions are obtained. The acetylated amines, monoglycerides and diglycerides of the acids are separated on silicone-treated paper with solvents containing varied amounts of methanol, acetic acid,  $\text{H}_2\text{O}$ ,  $\text{CHCl}_3$ , tetrahydrofuran and methyl cyanide. Autoradiography of the chromatograms reveals the separated materials.

S. BAAR

**2994. Detection of tea-seed oil in olive oil. Reliability of the Fitelson test.** A. Fichera and M. Zappalà (Lab. Chim. Provinciale, Messina, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (4), 342-345.—Sixty-four samples of olive oil and fourteen laboratory mixtures of olive oil with from 25 to 50% of arachis, rape-seed, cottonseed, sesame, soya-bean, grape-seed and tea-seed oils were submitted to the Fitelson test. Mixtures containing grape-seed oil gave a fleeting doubtful positive reaction, and tea-seed-oil mixtures gave a strong positive reaction. All the remainder gave clear negative results.

E. C. APLING

**2995. Laboratory methods for the determination of refining losses of oils and fats.** H. Pardun and O. Werber (Margarine-Union, Kleve, Germany). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 1010-1017.—Three laboratory methods were compared with actual plant losses on samples of arachis, cottonseed and soya oils. The methods used were (a) laboratory-scale application of the plant method (the A.O.C.S. cup method), (b) the determination of the theoretical losses from the content of  $\text{H}_2\text{O}$ , volatile matter, free fatty acids and phosphatides, and (c) the determination of neutral oil content by the Wesson method (*Oil & Fat Ind.*, 1926, **3**, 297) or by chromatography (*cf. Linteris and Hand-schumaker, J. Amer. Oil Chem. Soc.*, 1950, **27**, 260). The results obtained by the cup and Wesson methods can only be satisfactorily correlated when they relate to oils of equal phosphatide content.

S. BAAR

**2996. Vapour-phase chromatographic analysis of fats. I. Detection of [esters of] methanol and ethanediol.** S. Anselmi, L. Boniforti and R. Monacelli (Ist. Sup. di Sanità, Lab. Chim., Roma, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (4), 335-341.—Methods are described for the detection of ethanediol and methanol used for esterification of fatty acids in the adulteration of oils. Chromatograms were run in a Fractovap gas-chromatography apparatus, with a 200-cm column of succinic acid polyester supported on Celite C22, and with hydrogen gas as eluent. For the detection of glycols, saponify the oil with alcoholic KOH soln., acidify, and extract the fatty acids, neutralise the aq. layer, acidify with acetic acid and evaporate on a steam bath. Separate the glycerol and glycols from the salts by extraction with ethanol and evaporate to a syrup. Evaporate 0.02 ml at 230° on to the column operated at 170° with a flow pressure of 0.30 atm. Ethanediol, propane-1:2-diol and butane-2:3-diol give sharp peaks; glycerol is not detected. For the detection of methanol, 0.1 ml of the oil sample is evaporated at 300° on to the column operated at 200° with a flow pressure of 0.35 atm. In the presence of methyl esters a series of peaks are obtained corresponding to the methyl esters of the various fatty acids present.

E. C. APLING

**2997. Identification and determination of highly unsaturated fatty acids.** T. Miyakawa (Ind. Res. Inst. Osaka, Japan). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 850-855.—Poly-unsaturated fatty acids obtained from fish oils were separated by reverse-phase chromatography with undecane as the stationary phase and methyl cyanide and glacial acetic acid as the mobile phase in the proportions 7:5 to 1:2. These fatty acids were also fractionated by the differing solubilities of their lithium salts. The highly unsaturated fraction was further enriched by fractionation with urea at decreasing temp. This process was followed by low-temp. crystallisation over the range of 0° to -70°. The acids with the highest degree of unsaturation remained in the mother liquor. Some of these acids form critical pairs which cannot be separated by paper chromatography. Separation was, however, possible after hydrogenation with a palladium catalyst. It was then found that these highly unsaturated acids consisted of a mixture of  $\text{C}_{16}$  to  $\text{C}_{22}$  acids and a very small amount of  $\text{C}_{24}$  and  $\text{C}_{26}$  acids.

S. BAAR

**2998. Qualitative and quantitative determination of fatty acids in dehydrated castor oil by paper chromatography.** D. K. Chowdhury (Surendranath Coll., Calcutta, India). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 924-927.—Dehydrated castor oil was saponified, the soaps were hydrolysed and the free acids extracted and dried. All operations were carried out at low temp. and in the absence of oxygen. The composition of the acid mixture was determined by three methods. (a) Conventional methods were used for the determination of ricinoleic acid, conjugated and non-conjugated linoleic acids and oleic acid. (b) The fatty acids were acetylated, separated and identified by reverse-phase chromatography. (c) The acetylated acids were treated with maleic anhydride and the products again chromatographed. The product obtained from (c) was hydrogenated by the application of 15 to 100  $\mu\text{g}$  of palladium as catalyst at the origin of the chromatogram. All the acids were determined on the paper as their copper salts (*cf. Anal. Abstr.*, 1957, **4**, 2806). Comparison of the chromatograms makes possible the determination of ricinoleic, 9:11- and 9:12-linoleic, oleic, palmitic and stearic acids in castor oil.

S. BAAR

**2999. Quantitative paper chromatography of fatty acids. II. The photometric method.** A. Seher (Dtsch. Inst. Fettforsch., Münster, Westphalia, Germany). *Fette, Seif., Anstrichmitt.*, 1959, **61** (10), 855-859.—Fatty acids separated on paper chromatograms can be converted into heavy-metal salts. There is a stoichiometric relationship between the quantity of metal bound and the amount of fatty acid present. The copper salts can be prepared by treatment with cupric acetate and revealed with di-thio-oxamide or  $[\text{Fe}(\text{CN})_6]^{4-}$ . Theoretical considerations such as spot size, paper homogeneity, etc., and their influence on the direct photometry of the spots are fully discussed. Test analyses were carried out with stearic, palmitic, myristic, lauric and arachidonic acids. Provided that the conditions are precisely standardised and adhered to, an accuracy of  $\pm 3\%$  can be obtained.

S. BAAR

**3000. Short cuts to "lines of best fit" [in microbiological assays of vitamins].** F. W. Norris (Dept. of Appl. Biochem., Univ. of Birmingham, England). *Analyst*, 1959, **84**, 669-670.—A linear relationship between vitamin dose (ml) (V) and titre (ml) (T)



in microbiological assays may be represented by  $T = a + bV$ , where  $a$  is the intercept on the ordinate axis and  $b$  the slope of the line. The parameters  $a$  and  $b$  are calculated by the usual method of least squares, and the arithmetical labour in substituting experimental values in the formulae obtained is considerably simplified if the vitamin doses are added in simple amounts, e.g., 0, 0.5, 1, 1.5 and 2 ml. The values of  $a$  and  $b$  thus obtained when substituted in the linear equation provide an equation representing the best line, a line theoretically more accurate than one drawn by visual estimation between the scattered values of  $T$ .

A. O. JONES

**3001. The colour reaction between vitamin A and sulphuric acid.** R. Biffoli (Lab. Chim. Provinciale, Firenze, Italy). *Boll. Lab. Chim. Provinciali*, 1959, **10** (4), 380-388.—A soln. of vitamin A in ethanol reacts with 75%  $H_2SO_4$  to give an initial blue and finally (after 2 hr.) a stable, reproducible, crimson colour, with an absorption max. at 525 m $\mu$ . Beer's law is obeyed for vitamin-A concn. up to 50 i.u. per ml, and  $E_{1\text{cm}}^{1\%}$  is 1430. Ergocalciferol exhibits a similar colour reaction, but interference with the determination of vitamin A is negligible unless the concn. is  $> 100$  times that of the vitamin A.

E. C. APLING

**3002. Assay of vitamin-A oils. A report on three collaborative experiments.** E. Brunius (Nat. Inst. of Public Health, Stockholm, Sweden). *J. Ass. Off. Agric. Chem.*, 1959, **42** (4), 657-678.—The design and results of three experiments organised with the collaboration of 42 laboratories in 12 countries, by the Vitamin Assay Commission of the International Union of Pure and Applied Chemistry, are reported. The methods used were those recommended by the I.U.P.A.C. (I.U.P.A.C. report "The Assay of Vitamin-A Oils," Butterworths Scientific Publications, London, 1959). The correction formula derived for solutions of vitamin-A alcohol in isopropyl alcohol was  $E_{225}^{1\%}(\text{corr.}) = 6.815 \times E_{225}^{1\%} - 2.555 E_{310}^{1\%} - 4.260 E_{325}^{1\%}$ , and the factor used for conversion of the  $E_{1\text{cm}}^{1\%}$  325 m $\mu$  value into i.u. of vitamin A per g was 1830. Errors were computed for a probability level of 0.95 and the inter-laboratory errors of duplicates are quoted. The precision of spectrophotometric measurements on a standard solution of phenylazo-*p*-cresol in isopropyl alcohol was 1.3%. Loss of vitamin A in the preparation of the unsaponifiable matter varied from 1.2 to 1.5%, and in the chromatographic procedure was 2.4%, i.e., a total loss of from 3.5 to 4%. After application of the correction formula, the error for oils not requiring chromatography (category 1 oils) was increased from  $\approx 3$  to  $\approx 6$ . The error following chromatography and application of the correction formula (category 2 oils) was from 10 to 14%. Loss of vitamin A in the chromatographic procedure was substantially the same whether development of the column was followed by observation in u.v. light or by testing aliquots of the eluate with  $SbCl_5$ .

E. C. APLING

**3003. Detection of some vitamins of the B group by paper chromatography.** D. Blitek, K. Strzyga and H. Wardyńska (Zakład. Bad. Organoprep., Witamin Inst. Leków, Warszawa). *Acta Polon. Pharm.*, 1959, **16** (5), 389-393.—Thiamine, riboflavin, pyridoxine and nicotinamide are separated by the ascending technique on Whatman No. 1 paper. The paper is dried for 15 min. at 50°, then loaded with 0.01 ml of soln. ( $\approx 20 \mu\text{g}$  of vitamin) and again dried at 50° for 15 min. This procedure

improves the separation of thiamine and riboflavin. After development for 18 hr. at room temp., the chromatogram is dried at 50° for 15 min. and examined under u.v. light. Thiamine is detected with a modified Dragendorff reagent (orange spot), riboflavin with 0.05 N NaOH (yellow spot fluorescing strongly under u.v. light), pyridoxine with sulphuric acid soln. followed by  $Na_2CO_3$  soln. (yellow-orange spot), and nicotinamide with 1-chloro-2:4-dinitrobenzene followed by ethanolic KOH soln. (brown spot developing in 1 to 2 min.).  $R_F$  values are quoted for several solvent systems. The best was found to be *n*-butanol-acetic acid-water (4:1:5) (Partridge, *Biochem. J.*, 1949, **42**, 238).

W. ROUBO

**3004. Improvements in the agar-plate test for thiamine factors with *Lactobacillus fermenti* 36.** Z. G. Bánhidí (Wenner - Gren Inst. for Exp. Biol., Univ. of Stockholm, Sweden). *Analyst*, 1959, **84**, 657-659.—In agar-plate tests with thiamine in certain media recommended by various workers for thiamine assay the growth of *Lb. fermenti* was rather faint and ill-defined owing to the absence of some additional factor or factors not present in these media. The addition of Tween 80 overcame the deficiency and improved the density and visibility of the growth zones. The basal medium recommended is based on that of Sarett and Cheldelin (*J. Biol. Chem.*, 1944, **155**, 153), without alkali-treated peptone but with tryptophan, cysteine, ascorbic acid, pantothenic acid, Tween 80 and agar. Under certain conditions the thiazole moiety of the thiamine molecule can replace thiamine, but thiazole with its high  $R_F$  value can easily be separated from thiamine by paper chromatography.

A. O. JONES

See also Abstracts—2770, Determination of reducing sugars. 2843, Determination of dyes. 2869, Thallium in cereals. 2878, Reduced ascorbic acid in plants. 3020, Pesticide residues in foods. 3024, Hydrometers for milk.

### Sanitation

Analysis of air, water, sewage, industrial wastes, industrial poisons.

**3005. Determination of benzidine in the atmosphere.** V. Kratochvíl, J. Langner and R. Vlasák (Res. Inst. Org. Synth., Toxicol. Sect., Pardubice-Rybitví, Czechoslovakia). *Chem. Průmysl*, 1959, **9** (8), 402-406.—The methods described are based on the coupling of tetrazotised benzidine with (i) the sodium salt of 6-anilino-1-naphthol-3-sulphonic acid (I) or with (ii) *N*-ethyl-1-naphthylamine (II). The latter method is more sensitive and enables 0.001 mg of benzidine (III) to be determined in 50 ml, whereas the former method is very simple and suitable for routine control. *Procedure (i)*—Dilute 5 to 20 ml of the soln. containing 0.005 to 0.1 mg of III in 0.1 N HCl to 20 ml with the same solvent, cool to 0° to 5°, add  $NaNO_2$  soln. (1%) (1 ml) and after 10 min. add a cold soln. of I (dissolve 0.2 g of I in 100 ml of  $H_2O$ , cool with ice to 0° to 5° and mix with a cold soln. of 12 g of  $Na_2CO_3$  in 60 ml of  $H_2O$  and dilute to 200 ml) (5 ml), mix, and cool for 10 min. Then dilute at 20° with  $H_2O$  to 60 ml and after 30 min. measure the extinction at 520 m $\mu$ . Carry out a blank. Refer the results to a calibration curve. *Procedure (ii)*—To 5 ml of the soln. containing 0.005 to 0.05 mg of III in 0.1 N HCl add *N* HCl (2 ml), cool with ice to 0° to 5°, add  $NaNO_2$  soln.

(1%) (1 ml), and after 10 min. add sulphamic acid soln. (5%) (1 ml) and mix for 3 min. Add immediately a soln. of **II** hydrochloride (0.2% in 96% ethanol) (1 ml), dilute to 50 ml with ethanol and mix. After 1 hr. measure the extinction with the use of a S61 filter. Carry out a blank and refer the results to a calibration curve.

J. ZÝKA

**3006. Determination of chlorine dioxide in treated surface waters.** M. A. Post and W. A. Moore (Robert A. Taft San. Engng Center, Bureau of State Services, Dept. of Health, Educ., and Welfare, Cincinnati, Ohio). *Anal. Chem.*, 1959, **31** (11), 1872-1874.—To a 90-ml sample (or an aliquot diluted to 90 ml) in a 100-ml flask add 5 ml of buffer (243 g of Na acetate and 360 ml of acetic acid diluted to 1 litre) and 1 ml of  $\text{FeCl}_3$  soln. (0.01 mg of  $\text{Fe}^{III}$  per ml); dilute to vol. and add 0.4 ml of 8-amino-1-naphthol-3; 6-disulphonic acid (**I**) soln. (0.85 g dissolved in 500 ml of ethanediol and diluted to 1 litre). Mix, and set aside in the dark. Record the extinction at 525  $\mu$  in 5-cm cells against water 20 to 25 min. after the addition of **I**. In the presence of Cl, add 2 ml of malonic acid soln. (0.1%) after the acetate buffer and allow to stand for 20 min. before the addition of  $\text{FeCl}_3$  soln. Pyrophosphate and hexametaphosphate interfere, giving low results, and calibration should be made in the presence of comparable amounts. Nitrite gives high results but can be destroyed by the addition of 10%  $\text{H}_2\text{SO}_4$  (0.45 ml) and 1% sulphamic acid (1 ml) to the sample. Excellent results are reported for 0.05 to 1.0 mg of  $\text{ClO}_2$  per litre.

T. R. ANDREW

**3007. Determination of organic matter in water by oxidation with potassium permanganate.** A. L. Wilson (Central Electricity Res. Lab., Leatherhead, Surrey). *J. Appl. Chem.*, 1959, **9** (10), 510-517.—An alternative to the u.v. absorption method for the determination of fulvic acids in natural waters (*Anal. Abstr.*, 1960, **7**, 3008) is described. The sample is heated at 100° with dil.  $\text{H}_2\text{SO}_4$  soln. and 0.0125  $N$   $\text{KMnO}_4$  for 30 min., a known vol. of 0.0125  $N$  ammonium oxalate is added and the soln. is titrated with  $\text{KMnO}_4$ . High blanks are avoided by boiling out the flasks with dil.  $\text{KMnO}_4$  -  $\text{H}_2\text{SO}_4$  soln. before use. Fulvic acids accounted for between 68% and 94% of the total oxygen demand of the samples analysed; by dividing the results by a factor of 1.29, good agreement with the u.v. absorption results for fulvic acids was obtained.

P. D. PARR-RICHARD

**3008. Determination of fulvic acids in water.** A. L. Wilson (Central Electricity Res. Lab., Leatherhead, Surrey). *J. Appl. Chem.*, 1959, **9** (10), 501-509.—The u.v. absorption spectrum at 300  $\mu$  provides a measure of the fulvic acids present in natural waters; sensitivity, precision and accuracy are satisfactory. Since  $\text{Fe}^{2+}$  absorb at 300  $\mu$ , a correction is applied for the amount of  $\text{Fe}^{2+}$  present. In hard well-waters, silicate and nitrate also cause slight interference. *Procedure*—Add 10  $M$   $\text{HCl}$  (2 ml) to a 200-ml sample, warm to 70°, then cool. After 45 min. add 1% (v/v)  $\text{H}_2\text{O}_2$  soln. (0.5 ml) and set aside for 15 min. Filter through a No. 3 sinter [previously well washed with 1% (v/v)  $\text{HCl}$ ] and measure the extinction of the filtrate in 4-cm cells. Use 200 ml of de-ionised  $\text{H}_2\text{O}$  for a blank determination. A calibration curve is prepared from pure soln. of fulvic acids obtained from natural waters by concentration on anion-exchange resins.

P. D. PARR-RICHARD

**3009. Rapid test for amino acids for control of the functioning of biological purification of sewage waters.** G. van Beneden (CEBEDEAU, Liège, Belgium). *Bull. Cent. Belge Étude Docum. Eaux*, 1959, (107), 299-302.—Free and combined amino acids in water are detected and determined by the colour developed with ninhydrin on a spot of the hydrolysed material on filter-paper. *Procedure, qualitative*—A sample of filtered effluent or sewage (50 ml) is evaporated with 2.5 ml of conc.  $\text{HCl}$  to dryness. The residue is taken up in 0.5 ml of 0.2% aq.  $\text{NH}_3$  and 10 to 20  $\mu$  is spotted with a micropipette on to filter-paper. After being heated for 10 min. at 100°, the paper is sprayed with 1% ethanolic ninhydrin and reheated for 15 min. A clearer violet-red colour is obtained if the spot is subjected to electrophoresis on the paper for 16 hr. in a phosphate-acetate-borate buffer at pH 4.5, since impurities are left on the starting line. *Quantitative*—The test is made quant. by comparison with spots produced by similar hydrolysis of soln. of known concn. of peptone. Pure glycine or unhydrolysed peptone can be used, but the colour obtained is not quite the same as that from an effluent.

E. J. H. BIRCH

See also Abstracts—2662, Silica in water. 2754, Olefins in air.

#### Agricultural analysis

Soil, fertilisers, herbicides, pesticides, animal feeding-stuffs.

**3010. Accurate determination of boron in plant material.** R. J. Davidson and W. J. A. Steyn (Dept. of Chem., Rhodes Univ., Grahamstown, S. Africa). *J. S. Afr. Chem. Inst.*, 1959, **12**, 81-86.—The influence of pH, temperature and the drying period on the development of colour in the colorimetric determination of B with curcumin was investigated. Slight modifications were made to the method and a calibration curve was constructed. The precision of the method was tested by carrying out 20 separate determinations on a well-mixed citrus-leaf sample containing 109 p.p.m. of B. A percentage standard deviation of 1.9 was found. Phosphorus, Ca, Mg, K, S, Fe, Mn and Zn do not interfere. The method has been used for samples containing from 6 to more than 200 p.p.m. of B.

A. ABBOT

**3011. Spectrographic method for the analysis of plant material using sodium tetramethylenedithiocarbamate for the concentration of the trace elements.** A. Strasheim, D. J. Eve and R. M. Fourie (Nat. Phys. Res. Lab., S. African Council for Sci. and Ind. Res., Pretoria). *J. S. Afr. Chem. Inst.*, 1959, **12**, 75-80.—The Na tetramethylenedithiocarbamate-metal complexes were obtained from acid solution and dissolved in  $\text{CHCl}_3$ . Graphite containing Sn, the internal standard, was added to the partially evaporated solution. The dried extract was heated at 450° for 30 min. and mixed with  $\text{Li}_2\text{CO}_3$ . The sample was burnt to completion on the anode of a d.c. arc at 10 amp. The analytical lines were—Pb 2833.1, V 3185.4, Mo 3170.3, Mn 3044.6, Zn 3345.0, Co 3044.0 and 3453.5, Ni 3050.8 and Sn (internal standard) 3032.8 Å. Standards were prepared containing 3 to 1000 p.p.m. of Pb, V, Mo, Co and Ni, and 30 to 10,000 p.p.m. of Zn and Mn. The standard deviation from 18 determinations is given and the results are compared with those of other workers. The reproducibility is

not very good, but the use of Sn rather than Fe as internal standard obviates the accurate determination of Fe in the original sample. A. ABBOT

**3012. Residue analysis of gibberellic acid in grapes by bioassay and isotope methods.** G. Zweig and G. R. Cosens (Pesticide Residue Res. Lab., Univ. of California, Davis, U.S.A.). *J. Agric. Food Chem.*, 1959, **7** (10), 717-719.—Seedless-grape vines (2 varieties) were sprayed at 1 week after bloom with gibberellic acid, and with gibberellic acid labelled with  $^3\text{H}$ . The initial deposits on grape clusters, and residues at harvest 2 months later, were determined by bioassay, with dwarf maize seedlings as test plants, and by counting in a liquid scintillation spectrometer, with an internal standard. The extraction procedures were shown to be effective. Values by the bioassay method were consistently lower than those by the isotope method; the former method gives a more reliable level, and is preferred. M. D. ANDERSON

**3013. Modification of Thorn and Shu's method for organic carbon in soils.** J. H. Watkinson (Galloway Lab., Rukuhia Soil Res. Sta., Hamilton, New Zealand). *Analyst*, 1959, **84**, 629-632.—The sample mixed with a  $\text{KIO}_3$ - $\text{K}_2\text{Cr}_2\text{O}_7$  mixture is treated in the combustion flask with fuming  $\text{H}_2\text{SO}_4$  and  $\text{H}_3\text{PO}_4$  containing  $\text{KIO}_3$  from a reservoir surmounting the flask. The  $\text{CO}_2$  evolved is passed over heated copper gauze and silver wire and is absorbed in  $\text{NaOH}$  soln., from which it is liberated by addition of lactic acid and is then absorbed in standard  $\text{Ba}(\text{OH})_2$  soln. This is back-titrated with standard  $\text{HCl}$ , with thymolphthalein as indicator. A. O. JONES

**3014. Some factors in the determination of carbonate in soils.** J. H. Watkinson (Galloway Lab., Rukuhia Soil Res. Sta., Hamilton, New Zealand). *Analyst*, 1959, **84**, 659-660.—Refinements in Schollenberger's method (*Soil Sci.*, 1930, **30**, 307; 1945, **59**, 57) are described. It is shown that the amount of  $\text{CO}_2$  evolved from hydrolysis of organic compounds during 20 min. at  $75^\circ$  is  $\approx$  ten times that evolved at  $25^\circ$  and increases rapidly above  $45^\circ$ , so that reduced pressure should be used to permit boiling below this temp. It is shown also that moist and air-dried samples lose  $\text{CO}_2$  on storage, the loss depending on the moisture, the pH and the time of storage. A. O. JONES

**3015. Rapid vacuum-distillation method for determining carbonate in soils with ethylenediaminetetraacetic acid.** J. H. Watkinson (Galloway Lab., Rukuhia Soil Res. Sta., Hamilton, New Zealand). *Analyst*, 1959, **84**, 661-662.—The method described is a modification of Schollenberger's method (*Soil Sci.*, 1930, **30**, 307; 1945, **59**, 57). The acid is replaced by a soln. of EDTA (disodium salt) of pH 4.5, and the  $\text{Ba}(\text{OH})_2$  soln. is stirred continuously by means of a magnetic stirrer. The soil sample is heated with 0.5% w/v EDTA soln. in an evacuated apparatus at  $90^\circ$  to  $95^\circ$ , the  $\text{CO}_2$  evolved is absorbed in standard  $\text{Ba}(\text{OH})_2$  soln., and the excess of  $\text{Ba}(\text{OH})_2$  is back-titrated with standard  $\text{HCl}$ , with thymolphthalein as indicator. Hydrolysis of organic matter by EDTA soln. at  $95^\circ$  is slight and less than that in Schollenberger's method at  $30^\circ$ . A. O. JONES

**3016. Rapid, precise method for the determination of carbonates in soil and rocks. Modification of the Geisler-Maksimuk alkalimeter.** A. Dimitriu (Soil Chem. Lab., Bucharest). *Acad. R.P.R., Stud.*

*Cercet. Chim.*, 1959, **7** (3), 375-387.—A modification of the Schrötter apparatus is described and illustrated. Its use is discussed, and results, which agree well with those by the method of Knopp, are quoted for a number of soils and minerals. H. SHER

**3017. Determination of soil nitrates with a brucine reagent.** J. B. D. Robinson, M. de V. Allen and P. Gacoka (Coffee Services, Dept. of Agric., P.O. Box 4, Ruiru, Kenya). *Analyst*, 1959, **84**, 635-640.—An extract of the soil in  $\text{CaSO}_4$  soln. is treated with 2% sulphamic acid soln. to remove  $\text{NO}_3^-$ . A soln. of brucine in glacial acetic acid is then added and finally conc.  $\text{H}_2\text{SO}_4$ . The extinction of the cold liquid is measured in a long-cell absorptiometer with a blue No. 601 filter or spectrophotometrically at  $454 \text{ m}\mu$ . Nitrate N from 1 to 10 p.p.m. can be determined with a standard deviation of 0.4 p.p.m. The method is not satisfactory for  $\text{KCl}$  extracts of soil. A. O. JONES

**3018. Radiometric determination of potassium in industrial fertilisers.** S. Havelka and M. Raković (Dept. Spec. and Phys. Chem. Anal. Methods, Inst. of Chem. Technol., Prague). *Chem. Průmysl*, 1959, **9** (10), 509-511.—The influence of iodine and bromine on the radiation intensity was studied in applying the radiometric method to the determination of K in potassium salts, mainly in industrial fertilisers, with the use of Czechoslovak instruments. J. ZYKA

**3019. Determination of total organic chlorine in agricultural pesticides with sodamide.** A. Velnicek and L. M. Gavát. *Rev. Chim., Bucharest*, 1959, **10** (10), 582-585.—The proposed method is based on the dissolution of the substance in liquid  $\text{NH}_3$ , reduction with  $\text{NaNH}_2$  and titration of  $\text{Cl}^-$  with  $\text{AgNO}_3$ . *Procedure*—The sample (containing 0.001 equiv. of Cl) is dissolved in a Dewar flask in liquid  $\text{NH}_3$  ( $\approx 10 \text{ ml}$ ) added in 1-ml portions with continual shaking. If the sample is liquid, it is weighed in a phial, closed, and introduced into a Dewar flask; from 3 to 5 ml of liquid  $\text{NH}_3$  is added, and the phial is broken with a glass rod washed into the Dewar flask with liquid  $\text{NH}_3$ . The dissolution takes 2 to 3 min. and then  $\approx 1 \text{ g}$  of metallic sodium (free from oxide) is added cautiously in small portions. The soln. is at first deep blue, but with further addition of sodium it becomes more viscous and paler. A further addition of liquid  $\text{NH}_3$  (5 to 10 ml, in 1 to 2-ml portions) is made to re-dissolve the paste formed; the soln. then becomes clear and colourless. The excess of liquid  $\text{NH}_3$  is evaporated off by careful direction of a current of air into the Dewar flask on to the soln., so that the walls of the flask are not splashed; but, immediately above the level of the liquid, ice will form. The soln., together with the ice, is mixed with water, and an aliquot (rendered slightly acid with  $\text{HNO}_3$ ) is titrated with 0.1 N  $\text{AgNO}_3$ , with  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3$  as indicator. Some soln. are coloured yellow-brown, in which case the  $\text{Cl}^-$  are titrated potentiometrically in the soln. acidified with  $\text{H}_2\text{SO}_4$ , with a S.C.E.-silver wire electrode pair. The end-point is sharp. A comparison of results for 17 products tested as above and by the Stepanov method shows the present method to be much more accurate, the errors being generally within  $\pm 0.1\%$  and never  $> \pm 0.2\%$ . For compounds also containing sulphur, the sample treated with  $\text{NaNH}_2$  is boiled with 5 to 10 ml of  $\text{H}_2\text{O}_2$  (30%) under reflux for a few minutes before acidification and titration. The solubility of



some compounds in liquid  $\text{NH}_3$  is too low, and a list of 19 compounds is given, for which a mixture of ether and liquid  $\text{NH}_3$  can be used. H. SHER

**3020. Identification of pesticide residues in extracts of fruits, vegetables and animal fats. I. Chromatography.** W. P. McKinley and J. H. Mahon (Food and Drug Lab., Dept. of National Health and Welfare, Ottawa, Canada). *J. Ass. Off. Agric. Chem.*, 1959, **42** (4), 725-734.—Procedures are described for the extraction of pesticide residues with benzene or carbon tetrachloride, purification of the extracts by partition between *n*-hexane and methyl cyanide, adsorption of residual fat on a Florisil column, and paper chromatography on Whatman No. 1 paper with three solvent systems, (a) stationary phase, 2-phenoxyethanol (14% in ether); mobile phase, 2:2:4-trimethylpentane; (b) stationary phase, liquid paraffin B.P. (4% in ether); mobile phase, 40% aq. pyridine; and (c) stationary phase as for (b); mobile phase 70% aq. acetone.  $R_f$  values (referred to lindane as reference standard) are tabulated for 52 compounds. A number of variations of technique suitable for particular problems are discussed. In a study of over 1000 samples of fruit and vegetables, 80% of samples contained less than 1 p.p.m. of DDT and its degradation product DDE, and 3% contained more than the tolerance level of 7 p.p.m. of DDT.

E. C. APLING

See also Abstracts—2955, Hg in seed dressings. 2974, Chlorinated pesticides in foods.

## 5.—GENERAL TECHNIQUE AND APPARATUS

### General

**3021. Instrumentation in the foundry laboratory.** R. C. Rooney (B.C.I.R.A., Bordesley Hall, Alvechurch, Birmingham, England). *J. Res. Brit. Cast Iron Ass.*, 1959, **7** (14), 832-838.—Instruments in general use in foundry laboratories are compared and discussed, with special reference to optical techniques; equipment for emission spectroscopy and X-ray and  $\gamma$ -ray absorption and fluorescence is not considered. C. H. COWPER-COLES

**3022. Test-tubes and boiling-tubes.** British Standards Institution (2 Park St., London, W.1). B.S. 3218:1960. 5 pp.—Dimensions and tolerances are specified. N. E.

**3023. Plummets for the estimation of specific gravity.** A. D. Ainge (Ansells Brewery Ltd., Aston, Birmingham, England). *J. Inst. Brewing*, 1959, **65** (5), 429-431.—The construction is described of a glass plummet for the determination of sp. gr. by the principle of Archimedes. The difficulty of control of temp. is overcome by using a plummet which expands or contracts with variations of temp. to the extent of making it self-adjusting. N. E.

**3024. Density hydrometers for use in milk. Part 2. Methods.** British Standards Institution (2 Park St., London, W.1). B.S. 734:Part 2:1959. 29 pp.—Two procedures are specified for determining the density of milk so that it can be measured either with the milk fat wholly in the solid state or wholly in the liquid state. Tables are provided

relating the known fat content and density of milk with its solids-not-fat content. N. E.

**3025. Dilatometers for highly viscous systems. Recording and non-recording instruments.** J. F. Vocks and R. A. Crane (Western Div., The Dow Chemical Co., Pittsburgh, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1906-1908.—Two instruments are described that can be used for chemically reactive soln. with viscosities up to several thousand poises. K. A. PROCTOR

**3026. Simplified nitrometer for use in the Dumas nitrogen determination.** D. M. Miller and R. A. Latimer (Pesticide Res. Inst., Univ. Sub P.O., London, Ontario, Canada). *Anal. Chem.*, 1959, **31** (11), 1926-1927.—The nitrometer described requires no valve of any kind at the top of the measuring tube and is therefore simpler than any others previously described. The apparatus is illustrated. G. P. COOK

**3027. Gas analyser for determining the components of a gaseous mixture.** Z. V. Pakulyak. U.S.S.R. Pat. 119,376 (April 15, 1959).—A component in a gas mixture is measured by absorbing it in a suitable soln. (e.g.,  $\text{CO}_2$  in smoke is absorbed in alkali soln.), and by using an aerodynamic bridge to measure the fall of pressure caused thereby. The aerodynamic bridge is analogous to a Wheatstone bridge, with throttle valves instead of electrical resistances. The pressure difference is measured by a differential manometer. A diagram is given. C. D. KOPKIN

**3028. Automatic titrimeter for plotting true-scale titration curves.** H. Irving and L. D. Pettit (Inorg. Chem. Lab., South Parks Rd., Oxford, England). *Analyst*, 1959, **84**, 641-646.—The Honeywell-Brown recorder is modified to allow the chart and a micro-syringe delivering 0.005 to 0.02 ml of titrant per min. to be driven by the same motor. With suitable electrodes and an electronic pH meter, titration graphs (10 in.  $\times$  18 in.) can be plotted automatically. With a Vibron electrometer and pH meter, 0.003 unit of pH can be recorded and the pH scale can be extended to 64 in. The use of the apparatus is described for organic preparations requiring pH control, for kinetic studies at constant pH and for automatic titrimetry of various kinds. A. O. JONES

**3029. Automatic titration unit for chlorides in biological fluids.** K. G. Gadd (Public Health Lab., Federal Min. of Health, Lusaka, N. Rhodesia). *Lab. Practice*, 1959, **8** (10), 323-329.—An inexpensive instrument, based on the use of standard  $\text{AgNO}_3$  soln. and a burette assembly, is described and illustrated. The negative-going voltage appearing between immersed electrodes (platinum and silver) in the region of the end-point is applied to an amplifier system which operates a burette valve constructed from a dismantled 6-V vibrator of the type used in car radios. R. A. BRENNAN

**3030. Ammonia distillation apparatus (Markham). Microchemical apparatus.** British Standards Institution (2 Park St., London, W.1). B.S. 1428:Part B2:1960. 8 pp.—This specification was first published in 1953. The present revision contains a modification of the design of the condenser. N. E.

3031. A macro spinning-band distillation column. F. S. Jones and A. G. Nerheim [Res. and Devel. Dept., Standard Oil Co. (Indiana), Whiting, U.S.A.]. *Anal. Chem.*, 1959, **31** (11), 1929.—The efficiency of macro spinning-band columns can be increased by the use of Teflon bands of a particular design.

K. A. PROCTOR

3032. Rotatable fraction collector for a semi-micro distillation apparatus. L. G. Morrison (Smith & Nephew Res. Ltd., Hunsdon Labs, Ware, Herts.). *Lab. Practice*, 1959, **8** (10), 343-344.—Four collecting tubes (10 mm × 50 mm) are held in two neoprene discs (30 mm diam.) fitted on to a spindle which is a sliding fit into the sealed end of a B14 extended cone. The cone fits into a B14 socket on the bottom of the vacuum jacket, thus enabling the spindle assembly to be rotated from the outside.

R. A. BRENNAN

3033. Automatic distillation analysis. F. Salzer (Chem. Werke Huls A.-G., Marl, Krs. Recklinghausen). *Chem.-Ing.-Tech.*, 1959, **31** (6), 405-409.—Automatic distillation equipment is described, with operational details, whereby fractional distillation analysis of solvents, benzines and diesel oils according to A.S.T.M. specifications D86-54, D1078-49T and D158-54 may be made. The boiling temperatures obtained are compared with those given by a manually operated distillation apparatus. It is claimed that owing to its objective nature, the equipment is more reliable than manually-operated apparatus. From 4 to 6 units may be handled simultaneously by one operator.

G. P. MITCHELL

3034. Remarks on extraction equilibria. I. M. Oosting (Anal. Res. Inst. T.N.O., Rijswijk, Netherlands). *Anal. Chim. Acta*, 1959, **21** (4), 301-308.—Equations are derived to express (i) the concn. of the reagent anion and (ii) the extraction error, in the solvent extraction of metal chelates. H. N. S.

See also Abstracts—2616, 2751, Micro-hydro-generation apparatus.

#### Chromatography, ion exchange, electrophoresis

3035. Chromatography on polyamides (nylons). Z. Procházka (Dept. Nat. Products, Chem. Inst. Acad. Sci., Prague). *Chem. Listy*, 1959, **53** (9), 922-927.—A literature survey is presented. (25 references.) J. ZÝKA

3036. Infra-red cell for collecting chromatographic fractions. H. Szymanski, R. Povinelli, D. Stamiros and G. Lynch (Canisius College, Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (12), 2110.—The cell described resembles a standard i.r. gas cell, but has a heater coil which is used to activate some surface material held on a salt plate. The surface material used is Linde Molecular Sieve 13X, ground into the salt plate with a 400-mesh diamond spatula. Volatile material from the chromatographic column is sprayed directly on to the surface material and, even with volatile hydrocarbons, is held long enough for the spectrum to be obtained. Polar compounds, such as water and ammonia, give slight peak shifts when adsorbed, but these are not sufficiently large to distort the normal spectrum.

K. A. PROCTOR

3037. Two methods of detecting cations on paper chromatograms. A. Lewandowski (Dept. of Gen. Chem., Univ., Poznań). *Chem. Anal., Warsaw*, 1959, **4** (3), 539-544.—Cations that form insol. ppt. with  $\text{Na}_2\text{CO}_3$  may be detected on paper chromatograms by dipping the chromatogram for 10 sec. in  $\text{N Na}_2\text{CO}_3$ , washing the excess of  $\text{Na}_2\text{CO}_3$  away with  $\text{H}_2\text{O}$ , drying with filter-paper, then spraying with a mixture of  $\text{Na}_2\text{SO}_4$  and an indicator (bromocresol blue, phenol red or bromothymol blue). More than 40 cations were examined, but the method proved most successful for the detection of spots of Ba, Sr, Ca and Mg. Several cations can be located by the use of potassium ferrocyanide. The chromatogram is dipped in acid 0.1M  $\text{K}_4\text{Fe}(\text{CN})_6$ , rinsed in  $\text{H}_2\text{O}$  and then immersed in  $\text{CuSO}_4$  or  $\text{FeCl}_3$  soln. The spots become reddish-brown or blue, respectively, those due to Fe, Cu, Mo and  $\text{UO}_2^{++}$  are coloured instantly. The test is especially suitable for Ag, Bi, Cu, Cd, Sn, Mo, V, Ni, Co, Fe, Mn, Zn, Th and  $\text{UO}_2^{++}$ .

W. B. MIAKOWSKI

3038. New method of concentration of ions for paper chromatography. A. Lewandowski (Dept. of Gen. Chem., Univ., Poznań). *Chem. Anal., Warsaw*, 1959, **4** (3), 545-550.—Apparatus and procedure are described whereby a 1000-fold concentration of ionic substances from very dilute soln. can be achieved by passing the soln. through impregnated paper strips having the properties of ion-exchange resins. The cation soln. contained 0.1 to 1  $\mu\text{g}$  of metal per ml. The chromatographic solvent was transferred to the paper strips containing the concentrated ions by means of a piece of ordinary filter-paper. The addition of acid or base to the solvent liberates the adsorbed ions and regenerates the ion-exchange paper strips. Ion-exchange paper with secondary properties was also used; the exchanger was treated with ions able to form ppt. with the ions being concentrated, so that cations pptd. on the anionised paper combined with a suitable anion, while anions reacted with suitable cations on the cationised paper. In biological analyses it is convenient to use the anionised paper in the ferrocyanide form, as it combines with many trace elements, but not with Ca, Mg, K and Na, which usually form the main components of ash; the pptd. ferrocyanides are decomposed by alkali, and after washing the paper strips with  $\text{H}_2\text{O}$  the acid solvent is used. The disadvantage of this method is that its application is limited to ionic substances, but this may also be considered an advantage, because it enables the ions to be concentrated and separated from their mixtures with non-ionic substances.

W. B. MIAKOWSKI

3039. Method for the practical evaluation of chromatograms with the aid of diapositives. G. Halfter (J. R. Geigy A.-G., Grenzach, Baden, Germany). *Z. anal. Chem.*, 1959, **169** (6), 404-406.—A permanent standard for the determination of small amounts of dye-stuff intermediates is described. Known amounts of the test substance are chromatographed on clean textile fabric to give a graduated set of spots which are then made visible by chemical action. The spots are photographed in colour together with a scale, and the standard so produced is projected on to a screen for comparison with a test chromatogram.

P. D. PARR-RICHARD

**3040. Quantitative paper chromatography based on the sub-micro titration of derivatives containing nitro groups.** L. Blom and J. Caris (Centraal Lab., Staatsmijnen in Limburg, Geleen, Holland). *Nature*, 1959, **184** (Suppl. No. 17), 1313-1314.—Different carbonyl compounds in a complex mixture can be rapidly and quant. determined by converting them into the 2:4-dinitrophenylhydrazones and then obtaining a paper chromatogram of these on Whatman No. 1 paper by a modification of the method of Matthias (*Naturwissenschaften*, 1956, **43**, 351). The bands are cut out, concentrated into a small area if necessary, and put into a small flask containing O-free acetic acid and a suitable amount of Na acetate. An excess of 0.003 N  $\text{TiCl}_3$  ( $\approx 0.5$  ml) is then added, the mixture is stirred for  $\approx 5$  min. at  $50^\circ$  and, after making the soln. acid with HCl, the excess of  $\text{TiCl}_3$  is back-titrated with 0.03 N  $\text{FeCl}_3$  with thiocyanate as indicator. The results listed for eight simple aldehydes and ketones (20  $\mu\text{g}$  of each) show recoveries of 96 to 100%. The method is being extended to alcohols, phenols, amines and amino acids, the dinitro derivatives of which can be quant. reduced with  $\text{TiCl}_3$ . W. J. BAKER

**3041. Ester formation in acid-alcohol mixtures: effect on  $R_F$  values in paper chromatography.** R. P. Kendall and H. S. B. Marshall (Res. Dept., British Nylon Spinners, Ltd., Pontypool, Mon., England). *Chem. & Ind.*, 1959, (43), 1353-1354.—A direct correlation has been found between ester formation by organic acid-alcohol mixtures and changes in  $R_F$  value. Tabulated data for the hydrochlorides of hexamethylenediamine,  $\omega$ -aminoheptanoic acid and  $\omega$ -aminoheptanoic acid, show that the  $R_F$  values and ester content for the solvent system *sec*-butyl alcohol-formic acid-water (15:3:2) change rapidly over the first five days and remain constant thereafter, but for the system *n*-butanol-acetic acid-water (4:1:5) these values change steadily for three months. The first mixture would be satisfactory after a short ageing period, whereas the use of the second should be restricted to a few days after preparation. The concentrations of ester in the solvent systems were determined by vapour-phase chromatography. A dinonyl phthalate column was employed at  $100^\circ$ , and the amount of ester was calculated from the area under the chromatogram peak. E. G. CUMMINS

**3042. Quantitative evaluation of paper chromatograms and electropherograms without elution. II. Construction of a densitometer.** J. Mastner, F. Franěk and L. Novák (Res. Inst. Food Technol., Prague). *Coll. Czech. Chem. Commun.*, 1959, **24** (9), 2959-2966 (in German).—An automatic integration densitometer is described. By means of a small square slit and a two-dimensional movement of the chromatogram, good results can be obtained even when irregular spots are evaluated. The reliability of the apparatus was demonstrated with mixtures of amino acids and dyes on Whatman paper. J. ŽYKA

**3043. Advances in gas chromatography.** A. I. M. Keulemans (Insulindelaans 2, Eindhoven, Netherlands). *Z. anal. Chem.*, 1959, **170** (1), 212-219.—The theoretical and actual efficiencies of packed columns and Golay capillary columns are discussed. The efficiency of packed columns increases with the fineness of the packing and with reduction in the thickness of the film of liquid stationary phase. The minimum HETP achieved with a Golay column

is 0.5 mm, which does not approach the theoretical. With high-efficiency columns very small samples are used and highly sensitive detectors are required. G. BURGER

**3044. Conditions for achieving higher precision in gas-chromatographic analysis.** H. Oster (Siemens u. Halske, A.-G.). *Z. anal. Chem.*, 1959, **170** (1), 264-271.—Sources of error are discussed for 3 procedures, viz, (i) the sum of the peak heights is equated to 100%, (ii) an internal standard is included and (iii) the instrument is calibrated for the materials to be determined. G. BURGER

**3045. Programmed-temperature gas-chromatography apparatus.** S. Dal Nogare and J. C. Harden (Polychemicals Dept., E. I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1829-1832.—The apparatus described consists of an electrically heated column, a thermistor conductivity cell and bridge, and a linear temp. programmer with accessory equipment, and can be used for the rapid separation of polar and non-polar mixtures boiling between  $35^\circ$  and  $300^\circ$ . It can also be used for isothermic operation. K. A. PROCTOR

**3046. The polarity of stationary phases in gas chromatography.** L. Rohrschneider (Chem. Werk. Hüls A.-G.). *Z. anal. Chem.*, 1959, **170** (1), 256-263.—The relation between polarity and the ability to separate gaseous paraffins and olefins has been investigated for 23 stationary phases. A graphic method for calculating the separating efficiency of combined columns is described. G. BURGER

**3047. Criteria for the separating efficiency of stationary phases in gas chromatography.** D. Jentzsch and G. Bergmann (Inst. f. Spektrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck). *Z. anal. Chem.*, 1959, **170** (1), 239-255.—The expression due to Herington ("Vapour Phase Chromatography," Butterworths Sci. Publ., London, 1957, p. 5), relating the ratio of retention volumes to the ratio of the vapour pressures and the activity coeff. of the components at infinite dilution in the stationary phase, is discussed. An expression for the efficiency of a column is derived which takes account of the overlapping of the zones and has been tested with 16 aromatic hydrocarbons and 5 stationary phases at  $100^\circ$ ,  $130^\circ$  and  $150^\circ$ . G. BURGER

**3048. Use of two or more internal standards in gas chromatography.** E. H. Lee and G. D. Oliver (Plastics Div., Monsanto Chemical Co., Texas City, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1925.—If the internal standard system of calibration is being used and the retention times of sample peaks are very different, then accuracy may be improved by using more than one internal standard. These standards and their concn. may be chosen so that their magnitude and peak position approach those of the desired unknowns. Small amounts of styrene (0.1 to 3%), benzene and toluene (0.02 to 0.5%) have been determined in ethylbenzene with *n*-decane as internal standard for styrene and 2:2:5-trimethylhexane for benzene and toluene. K. A. PROCTOR

**3049. Carrier gas and sensitivity in gas chromatography.** E. M. Fredericks, M. Dimbat and F. H. Stross (Shell Devel. Co., Emeryville Lab., Calif., U.S.A.). *Nature*, 1959, **184** (British Association



Suppl.), B.A. 54.—Under practical conditions in which the filament temp. in a thermal conductivity detector is held constant, He as a carrier gas is nearly 10 times as sensitive as Ar. A bridge current of 350 mA in He gives the same filament temp. as one of 150 mA in N, CO<sub>2</sub> or Ar, in which gases a bridge current of 350 mA would cause the filament to burn out.

H. F. W. KIRKPATRICK

**3050. The separating efficiency of silica gels in gas chromatography.** G. R. Schultze and W.-J. Schmidt-Küster (Inst. f. Erdölforschung, Hannover). *Z. anal. Chem.*, 1959, **170** (1), 232-238.—The effect on the resolution of gas mixtures of drying the silica gel at different temp. and of loading with a liquid stationary phase was investigated, with methane as carrier and test mixtures of N, H, CO, ethane and ethylene. The best results at room temp. were obtained with fine-pored silica gel dried at 250° for 24 hr. and loaded with 7% of dibutyl phthalate.

G. BURGER

**3051. A glow discharge detector for gas chromatography.** R. A. Basson, C. R. de Wet, W. Nel and V. Pretorius (Dept. of Phys. Chem., Univ. of Pretoria, S. Africa). *J. S. Afr. Chem. Inst.*, 1959, **12**, 62-68.—The effects of a number of parameters on the sensitivities of a flame ionisation detector are described.

E. G. CUMMINS

**3052. Smoke-eliminating device for a vapour-phase chromatographic-fraction collector.** P. Kratz, M. Jacobs and B. M. Mitzner (Instrumental Analysis Lab., van Ameringen-Haebler Inc., Rose Lane, Union Beach, N.J., U.S.A.). *Analyst*, 1959, **84**, 671-672.—When the receiver is chilled in an ice bath as a means of increasing the efficiency of collection, fractions with a b.p. > 175° tend to produce a smoke of charged particles on the walls of the chilled receiver. By application of the principle of the Cottrell precipitator, collection of the smoke-forming fractions is substantially quantitative. High-tension current is supplied to a copper coil encircling the container, and the silent discharge across the exit gas to a copper electrode in a glass tube inserted in the container condenses and precipitates the smoke. The device cannot be used when H is the carrier gas, or in any conditions when sparking might be dangerous.

A. O. JONES

**3053. Condensing system for determination of trace impurities in gases by gas chromatography.** N. Brenner and L. S. Ettre (The Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1815-1818.—The simple accessory described consists of a condenser column which can be packed with selected column materials and which can be substituted for the sampling volume tube in the Perkin-Elmer precision gas-sampling system. By using a sufficiently large sample vol., the min. detectability of the system is about 0.1 p.p.m. Various applications are discussed.

K. A. PROCTOR

**3054. Anomalous calibration curves in gas chromatography.** A. Weinstein (Dept. of Fuel Technol., State Univ., University Park, Pa., U.S.A.). *Chem. & Ind.*, 1959, (43), 1347-1348.—A tentative explanation is given of the lack of recognisable peaks at low pressures (< 5 mm) of CO in experiments carried out with a 15-ft. column packed with 30 to 70-mesh Linde Molecular Sieve No. 5A, dehydrated for 24 hr. at 240° in vacuo, and with

argon as carrier gas. The reported increase in retention time of CO with decrease in water content of the molecular sieve has been linked with the baring of active sites as well as with increase in surface area. It is suggested that progressive loss of a small sample to active sites with their lower rate of desorption can cause disappearance of measurable peaks.

E. G. CUMMINS

**3055. Large-scale density-gradient electrophoresis. II. Simple experimental technique securing perfectly stable zones and full utilisation of the separation capacity of a density-gradient column.** H. Svensson and E. Valmet (LKB-Prod. Fabriks-aktiebolag, Stockholm, Sweden). *Sci. Tools*, 1959, **6** (2-3), 13-17.—A gradient mixing device with two mixing compartments coupled in series is illustrated. Useful only for descending electrophoresis, the apparatus provides easily reproducible experimental conditions. Theoretical considerations show that six desirable conditions can be satisfied. (i) The sucrose concentration gradient should be constant at the point where the protein concentration has its maximum negative gradient (for inhibition of droplet sedimentation). (ii) An initial positive gradient throughout the column should be provided. (iii) The sucrose concentration gradient should be strong enough to carry and stabilise the migrating protein zones. (iv) The density gradient due to the sucrose should be fully utilised. (v) The volume of the initial zone should stay below such a fraction of the whole column volume as is compatible with the desired fineness of the separation. (vi) The initial and final sucrose concentrations in the stream from the mixer should be compatible with those of the light and heavy buffers in the column. Application of the method to ascending electrophoresis is discussed.

E. G. CUMMINS

See also Abstracts—2762, Stationary phase for gas chromatography. 2783, Gas-chromatography temp. control. 3098, 3100, Radioactivity of chromatograms.

### Optical

**3056. Apparatus and method of converting X-ray diffraction patterns.** Esso Research & Engng Co. [Inventor: J. E. Lloyd]. Brit. Pat. 829,040; date appl. 30.1.57.—Printed X-ray diffraction patterns of a known substance are converted into a photograph suitable for comparison with X-ray diffraction patterns of an unknown substance by projecting a beam of light of variable intensity through a slit on to a strip of unexposed photographic film so as to produce a pattern of lines on the developed film such that their disposition would be the same as an X-ray diffraction pattern obtained from the known substance. The intensity of the illumination of the slit for each line is directly proportional to the corresponding value of intensity of the printed X-ray diffraction data and the diffraction pattern of lines on the film is the same size as the X-ray diffraction pattern of the unidentified substance.

J. M. JACOBS

**3057. Flame photometry as an instrumental micro-analytical method.** J. Ramirez-Muñoz (Univ. de Santander, Bucaramanga, Colombia). *Rev. Univ. Ind. Santander, Colombia*, 1959, **1** (1), 15-27.—After a review of the principles of flame photometry, the working range for this method is given and compared with the ranges of classical, absorption and spectrographic methods. The quantitative

concepts of minimum concn. limit, minimum volume limit and minimum mass limit are discussed, and the qualitative and quantitative sensitivity limits for 46 elements are given. G. H. FOXLEY

**3058. Light detectors for vacuum spectroscopy.** E. Lüscher (Tech. Hochsch., Lausanne, Switzerland). *Chimia*, 1959, **13** (9), 284-285.—A review of photographic, photo-electric and electronic detectors is presented, with 18 references. E. G. CUMMINS

**3059. Spectrographs and monochromators for vacuum spectroscopy.** E. Lüscher (Tech. Hochsch., Lausanne, Switzerland). *Chimia*, 1959, **13** (9), 277-283.—A review is presented, with 45 references, and a discussion is included of the properties of materials transparent down to 1000 Å and reflecting down to 400 Å, and their use in prisms and gratings, together with a full theoretical treatment of concave gratings. E. G. CUMMINS

**3060. New procedure for spectral gas analysis.** W. Koch, S. Eckhard and F. Stricker (Max-Planck Inst. f. Eisenforsch., Düsseldorf, Germany). *Angew. Chem.*, 1959, **71** (17), 545-549.—When gases are excited under standard conditions by means of a high-frequency discharge, the max. intensity of the emission bands of a gas is proportional to its concn. Mixtures (0.15 ml) of H, N and CO extracted from steel are thus analysed at 0.1 to 0.2 torr in the visible region of the spectrum in 2.5 to 4 min. with the aid of a recording instrument. The wavelengths used are 4278 Å for N, 4340 and 4861 Å for H, and 4835 Å for CO. The procedure requires careful calibration but has high sensitivity. The method is applicable to other gas mixtures and can be used for continuous analysis. J. P. STERN

**3061. A comparison of carbon and graphite electrodes.** J. W. Mellichamp and J. J. Finnegan (U.S. Army Signal Res. and Dev. Lab., Fort Monmouth, N.J., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (5), 126-130.—The physical properties of carbon and graphite are compared and consumption rates in the arc are investigated. The data are discussed with particular reference to choice of material for electrodes in spectrographic analysis. P. T. BEALE

**3062. Time-lapse emission spectra using a rotating slotted disc and stationary emulsion.** W. L. Dutton and R. C. Hirt (Central Res. Div., Amer. Cyanamid Co., Stamford, Conn., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (5), 120-122.—The racking of the photographic plate during exposure produces a stepped spectrum which is useful in qualitative analysis since concentration sensitivity is greater owing to a lower background, and the time-positions of the spectral lines correspond to the boiling-points of the emitting elements. The new device consists of a slowly rotating disc with a series of concentric slots which is placed at the slit of a stigmatic spectrograph, the plate remaining stationary. The resulting spectra have better definition and record 100% of the exposure time. P. T. BEALE

**3063. A recording Raman spectrograph.** P.-O. Kinell (Inst. Phys. Chem., Univ., Uppsala, Sweden). *Ark. Kemi*, 1959, **14** (4), 337-351.—A detailed description (illustrated) is presented of a recording Raman spectrograph on which direct and photographic records can be obtained. The instrument

was used to determine wave numbers, with an accuracy of  $\pm 1 \text{ cm}^{-1}$ , and Raman lines of liquid  $\text{AsCl}_3$  and liquid  $\text{POCl}_3$ . The use of Polaroid cylinders round the Raman tube for depolarisation measurements is discussed. S. BAAR

**3064. Simple device for taking the Raman spectra of solids. Raman spectra of urea molecular compounds.** B. Schrader, F. Nerdel and G. Kresze (Org.-chem. Inst., Tech. Univ., Berlin-Charlottenburg). *Z. anal. Chem.*, 1959, **170** (1), 43-55.—With the apparatus described the sample may be in the form of powder, tablets of pure material or tablets with KBr. The apparatus is built as a unit for mounting on an optical bench, and is interchangeable with an apparatus for use with liquid samples. Either device can be fitted to a spectrometer without further adjustment. A minimum-grain enlarger with a paper carriage moving parallel with the spectral lines is described. The results obtained with molecular compounds of urea and thiourea and with occluded substances are discussed. G. BURGER

**3065. Precision in X-ray emission spectrography. Background present.** P. D. Zemany, H. G. Pfeiffer and H. A. Liebhafsky (General Electric Co., Schenectady, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1776-1778.—From a consideration of the probability theory and the theory of errors the precision in X-ray spectrography can be predicted and controlled, under proper conditions, even when the background is significant. These findings are supported by 90 results on a spot containing  $< 2 \times 10^{-7} \text{ g}$  of Zn and by 216 results on a spot containing  $4 \times 10^{-8} \text{ g}$  of Sr. K. A. PROCTOR

**3066. A cooled sample-holder for the X-ray spectrograph.** C. W. Diggins, jun., J. R. Lindley and B. H. Eccleston (Petroleum Exp. Sta., U.S. Dept. of the Interior, Bartlesville, Okla., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1928.—In the holder described, all parts exposed to the X-ray beam are of pure aluminium; the sample vol. is as small as practicable without undue reduction of intensity; a thin plastic film can be attached as a sample cover, if necessary, and the height of the sample with respect to the beam is adjustable. The holder is easily cleaned and rapidly attains thermal equilibrium. It has been used primarily for internal standard methods, but provision is made for filling to a reproducible level when used with external standard methods. K. A. PROCTOR

**3067. X-ray Rayleigh scattering method for analysis of heavy atoms in low Z media.** C. A. Ziegler, L. L. Bird and D. J. Chelek (Tracerlab Inc., Waltham, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1794-1798.—The dependence of an X-ray coherent scattering cross-section on the atomic number of the scattering atom is the basis of the method described. Advantages of this technique, which can be made self-monitoring, over conventional X-ray methods, and applications in the chemical processing industry are discussed. K. A. PROCTOR

**3068. A possible solution to the matrix problem in X-ray fluorescence spectroscopy.** E. J. Felten, I. Fankuchen and J. Steigman (Polytech. Inst. of Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1771-1776.—Matrix effects are reduced by

extrapolating fluorescent-intensity ratios in binary systems to zero sample-thickness. Extrapolated ratios for pairs of transition metals are related to the molar fraction ratios.

K. A. PROCTOR

**3069. Measurement of fluorescence spectra with spectrophotometers and comparison standards.** E. Lippert, W. Nägele, I. Seibold-Blankenstein, U. Staiger and W. Voss (Phys. Chem. Lab., Tech. Hochschule, Stuttgart). *Z. anal. Chem.*, 1959, **170** (1), 1-18.—The design features necessary in a fluorescence spectrometer are discussed. The Perkin-Elmer model 13 U spectrometer with reflection attachment is described. A list of standard soln. with their fluorescence spectra is given. Comparison with a standard eliminates several sources of error in the measurement of intensity.

G. BURGER

**3070. Methods of indirect spectrophotometry.** C. N. Reilley and G. P. Hildebrand (Dept. of Chem., Univ. of N. Carolina, Chapel Hill, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1763-1766.—The relative merits of several methods of measuring photometrically the extent of fading in indirect spectrophotometry are evaluated. As examples of such methods the determinations of Mg with Calcon (C.I. Mordant Black 17) and Ca with Mg-EDTA are described.

K. A. PROCTOR

**3071. New developments in instrument technology for infra-red spectroscopy.** G. Bergmann (Inst. f. Spectrochem. u. angew. Spektroskopie, Dortmund-Aplerbeck). *Z. anal. Chem.*, 1959, **170** (1), 66-78.—General criteria for the evaluation of instruments are discussed. An increase in theoretical resolving power beyond that necessary to achieve the maximum actual resolution is advantageous because an increase in the signal-to-noise ratio follows. The relevant design features are indicated. Available light sources for the near and medium infra-red cannot be much improved. Zirconium point-source lamps are increasingly used with off-axis elliptical or toroidal mirrors. The sensitivity of the older types of detector can only be improved by the use of low temp. (liquid He). The long-wave sensitivity of semi-conductors has been improved with the introduction of indium antimonide and germanium. Other improved components are optical filters and recorders with automatic amplification control. In the long-wave region improvements are directed to the elimination of scattered light of shorter wavelength. Interference spectrometers, at present laboratory-made only, are characterised by very high resolution and light transmission. Two new interference spectrometers use the Michelson principle with amplitude- or frequency-modulation. Analogue computer techniques have been developed. (27 references.)

G. BURGER

**3072. A new i.r. spectrometer in the 12.5 to 25- $\mu$  region.** N. L. Alpert, F. Behnke and P. A. Strauss (The Perkin-Elmer Corp., Norwalk, Conn., U.S.A.). *Appl. Spectroscopy*, 1959, **13** (5), 130-132.—A new version of the Perkin-Elmer Model 137 i.r. spectrophotometer, incorporating a KBr prism, is described. Typical spectra in the 12.5 to 25- $\mu$  region are shown and useful applications are discussed, such as the simple identification of straight-chain hydrocarbons and the differentiation between mono- and di-sulphides.

P. T. BEALE

**3073. Infra-red spectroscopy of aqueous solutions.** J. D. S. Goulden (Physics Dept., Nat. Inst. Res. Dairying, Univ. of Reading, England). *Spectrochim. Acta*, 1959, (9), 657-671.—Absorption spectra of aq. soln. can be obtained in the regions of wavelength  $< 2.5 \mu$ , 3.5 to 5.8  $\mu$ , and 6.5 to 10.5  $\mu$ . Suitable window materials for the construction of cells of 12 to 75- $\mu$  path length, are discussed. Publications by other workers in this field are reviewed and new experimental data are given on the application of this technique to the study of various inorganic, organic and biological materials. A detailed examination of sodium borate soln. and quantitative measurements of valine-norvaline and glucose-galactose mixtures illustrate the usefulness of the technique.

P. T. BEALE

**3074. Novel micro and semi-micro pelleting technique for infra-red spectroscopy.** F. Bissett, A. L. Bluhm and L. Long, jun. (U.S. Army Quartermaster Res. and Engng Center, Natick, Mass., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1927.—The technique described, which can be used with almost any die, consists essentially in using a matrix of KBr to confine a dispersion of the sample to a small aperture in a metal disc embedded in the matrix. It is especially useful in the preparation of vacuum-formed micro-samples 0.5 mm in diameter.

K. A. PROCTOR

**3075. Advantages and limitations of the potassium bromide method of preparing samples for infra-red spectroscopy.** H. Röpke and W. Neudert (Schering A.-G.). *Z. anal. Chem.*, 1959, **170** (1), 78-95.—The KBr pellet method is more universally applicable than any other method of preparing solid samples, as KBr is almost completely inactive towards the infra-red. All solid and viscous materials can be compared and quant. determinations can be made within 1% on samples as small as 0.01 mg. The main disadvantages arise from the difficulty of removing traces of H<sub>2</sub>O from KBr and from anomalies due to polymorphism, reaction with water, evaporation or reaction of impurities in the sample, change in mol. wt., reaction with KBr, formation of mol. compounds, decomposition and dehydrogenation, all of which can be induced by pelleting. Examples are discussed. (51 references.)

G. BURGER

**3076. Interaction between sugars and alkali halides in pressed discs.** V. C. Farmer (Dept. of Spectrochem., Macaulay Inst. for Soil Res., Aberdeen, Scotland). *Chem. & Ind.*, 1959, (42), 1306-1307.—Changes in i.r. absorption spectra when sugars and certain steroids are ground with potassium halides of differing degrees of purity are discussed. In some cases, changes are caused by the formation of sodium complexes, in others by conversion to the anhyd. state. Steroids are converted to this state by mechanical grinding alone. Potassium halides for i.r. spectroscopy should contain  $< 0.01\%$  of sodium.

P. D. FARR-RICHARD

**3077. Infra-red spectra in the solid state: anomalous hydroxyl-group absorption in potassium halide discs.** R. A. Durie and J. Szweczyk (Commonwealth Sci. Ind. Organisation, Coal Research Section, Sydney, Australia). *Spectrochim. Acta*, 1959, (8), 593-597.—When the i.r. KCl disc technique is employed, a persistent OH absorption occurs at 3380  $\text{cm}^{-1}$  in the spectra of



some non-hydroxylic polynuclear aromatic hydrocarbons, which cannot be removed by heating. Hydroxyl groups are introduced into KCl by grinding in the presence of atmospheric moisture, and the effect of these is enhanced by the presence of highly condensed aromatic compounds, e.g., 1:2-benzanthraquinone or dibenzanthrone. It may be prevented by preparation of KCl and sample mixtures under volatile non-polar solvents, e.g.,  $\text{CCl}_4$  or  $\text{CS}_2$ . The polynuclear hydrocarbon enhancement is not understood.

G. P. MITCHELL

**3078. Apparatus for following reactions in an infra-red spectrophotometer.** J. W. Forbes and A. Telfer (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1904-1906.—The design of the apparatus is such that the composition of the soln. in a small reaction reservoir can be varied, and either periodically or continually examined by i.r. spectroscopy. It is particularly useful for studying reaction rates, equilibrium constants, mol. formulae of complexes and some polymerisations, and can be used in differential measurements to prepare soln. of the proper concn. directly in the spectrophotometer.

K. A. PROCTOR

**3079. Rapid photo-electric colorimetric determination of fluoride.** J. A. C. van Pinxteren (Farm. Lab., Rijksuniv., Utrecht, Netherlands). *Pharm. Weekbl.*, 1959, **94** (20), 649-655.—An instrument is described and illustrated which comprises two equal and opposite wedge-shaped glass cells, which can be placed together to form a rectangular cell 12 cm long and 5 cm deep internally, with a combined effective light-path of 2 cm. A movable light-source and photo-cell permit the photo-current to be measured at any point along the length of the cell, the sensitivity being increased by means of an electronic amplifier, and the photo-current being balanced by means of a potentiometer. Into the two halves (A and B) of the cell are placed two soln. of known concn. ( $C_A$  and  $C_B$ ) of the substance to be measured, and the photo-current is balanced with the photo-cell at the mid-point of the long side of the cell. The soln. in B is then replaced by the unknown soln., and the photo-cell and light-source are then moved until the photo-current is again balanced. From the known concn.  $C_A$  and  $C_B$  and the distance traversed by the photo-cell, the unknown concn. can be calculated. The manipulation and calculation are described, and the instrument is applied to the determination of  $\text{F}^-$  in water by the method of Megregian (*Anal. Abstr.*, 1954, **1**, 2676) which employs the zirconium lake of Eriochrome cyanine R (C.I. Mordant Blue 3) and by the Na alizarinsulphonate method.

M. J. MAURICE

**3080. High-temperature cell assembly for spectrophotometric studies of molten fluoride salts.** J. P. Young and J. C. White (Anal. Chem. Div., Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1892-1895.—The assembly described, in which temp. as high as  $780^\circ$  can be maintained, fits the cell-housing assembly of the Cary Model 14-M recording spectrophotometer and is designed for easy conversion from normal to high temp. use. The exterior is water-cooled. A crystalline magnesium oxide cell is described as well as a pendent-drop arrangement in which the molten salt is confined by a platinum ring, coil or cylinder, thus virtually eliminating corrosion effects.

K. A. PROCTOR

**3081. Direct quantitative diffractometric analysis.** P. P. Williams (Dominion Lab., Wellington, New Zealand). *Anal. Chem.*, 1959, **31** (11), 1842-1844.—In the method described, the sample is mounted on a metal surface and measurements are made of the intensities of reflections from the metal, with and without the sample in place, so that no reference to an internal standard is necessary. Results of analyses of NaF and quartz mixtures are accurate to within about  $\pm 4\%$  of the total wt. of the mixture.

K. A. PROCTOR

### Thermal

**3082. A study of ebullioscopic molecular-weight methods.** J. V. Kennedy, R. J. Fries, L. J. Sullivan and C. B. Willingham (Mellon Inst., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1884-1889.—The precision and limitations of two techniques (the ebullioscopic constant and the comparative standard method) have been evaluated by using pure hydrocarbons and a few non-hydrocarbons as solutes. The ebullioscopic constant is independent of mol. wt. and solute type at infinite dilution, and mol. wt. can be obtained to within 1 to 2% of the true wt. The comparative method, with an internal or external standard, may yield reliable results to within 2-5% if suitable precautions are observed.

K. A. PROCTOR

**3083. Halogens and sulphur. Combustion train (micro-Grote). Microchemical apparatus.** British Standards Institution (2 Park St., London, W.1). B.S. 1428: Part A4:1960. 11 pp.—Components are specified for the micro-Grote determination of halogens and sulphur in organic compounds.

N. E.

**3084. Development of a thermobalance for use under pressure.** P. Bastien and M. Colombié *Métaux (Corrosion-Ind.)*, 1959, **34**, 447-450.—The gravity-type thermobalance described and illustrated permits corrosion tests on metals and alloys to be made, e.g., in  $\text{CO}_2$ , H or  $\text{H}_2\text{S}$ , at high temp. and at pressures from  $5 \times 10^{-4}$  torr to 30 kg per sq. cm. The sample is placed at the upper end of a silica rod enclosed in a nickel-chromium steel tube, which is surrounded by an electric furnace and well insulated from the moving parts of the balance. These are enclosed in a stainless-steel sheath (kept at  $\approx 25^\circ$ ) and comprise a horizontal needle, with a bifilar suspension (tungsten) and damping and counterpoise control, provided with a concave mirror whereby displacements are recorded optically and amplified electronically onto a screen. Charging and discharging under pressure are effected electromagnetically. The sensitivity is  $\approx 0.1$  mg, each 3-mm movement of the spot on the scale corresponding to 1 mg. The max. heating rate is  $\approx 600^\circ$  per hr. and the max. permissible temp. at the higher pressures is  $700^\circ$ .

W. J. BAKER

### Electrical

**3085. Galvanic cells sensitive to traces of gaseous, liquid or solid substances.** A. Berton. *Chim. Anal.*, 1959, **41** (9), 351-358.—A system is described consisting of a ring electrode supporting a drop of electrolyte, with a second electrode dipping into the drop. Provision is made for replenishing the drop and the unit is enclosed in a glass envelope with

inlet and outlet for the gas under observation. If the two electrodes are of platinum and the liquid is water, the unit can be used as a conductivity cell, sensitive to the presence of soluble ionisable vapours in the gas under test. By using dissimilar electrodes and a reactive electrolyte the unit may be used as a galvanic cell sensitive to certain vapours, e.g., platinum|H<sub>2</sub>SO<sub>4</sub>|lead, sensitive to NH<sub>3</sub> vapour, and platinum|K<sub>2</sub>Fe(CN)<sub>6</sub>|lead, sensitive to alcohols and acetone. Potential applications for gas chromatography or physiological investigations are suggested.

T. R. ANDREW

**3086. A modified electrolytic cell with mercury cathode.** B. Kysil (Chem. Lab. SONP Kladno, Czechoslovakia). *Chem. Listy*, 1959, **53** (9), 950-951.—A new type of electrolytic cell with a mercury cathode is described, which permits the use of small vol. (10 to 20 ml) of the sample soln. and removal of the required vol. of the electrolysed soln. without separating mercury from the cell. The device described was used for the determination of B, Al and Ti in steel and of Mg in cast iron. J. ZÝKA

**3087. Linear polarographic voltages at high cell-currents.** D. M. Kern (Steele Chem. Lab., Dartmouth College, Hanover, N.H., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1930.—A device to correct for internal resistance drop and anode-pool potential and identical in principle to that of Oka (*Anal. Abstr.*, 1959, **6**, 1165) has been developed, but with an additional feature which corrects for non-linear voltage at high currents. K. A. PROCTOR

**3088. Influence of gold in a mercury electrode on electrode processes.** W. Kemula, Z. Kublik and Z. Galus (Inst. of Phys. Chem., Polish Acad. of Sci., Warsaw). *Nature*, 1959, **184** (British Association Suppl.), B.A. 56-57.—Preparation of a hanging-drop mercury electrode on gold wire introduces a variation in the electrode process owing to the formation of intermetallic compounds with Au on the surface of the electrode. Such an electrode is essentially an amalgam electrode and the effect has been evaluated with Zn by using various concn. of Au in mercury (0.001, 0.01 and 0.1%) for the electrodes previously described (Kemula and Kublik, *Anal. Chim. Acta*, 1958, **18**, 104) which are not subject to this effect.

H. F. W. KIRKPATRICK

**3089. Capillary pH electrode.** R. H. Wilkinson (Hosp. for Sick Children, Gt. Ormond St., London). *J. Sci. Instrum.*, 1959, **36** (10), 424-425.—A thin glass capillary (140 mm × 1 mm ext. diam.) is enclosed in a glass envelope and the annular compartment is filled with 0.1 N HCl into which dips a silver chloride electrode. By means of a syringe, the sample soln. is forced through the pH capillary from one end to make contact with the satd. KCl soln. of the reference electrode at the other end. The precision for venous blood is ± 0.0015 pH unit over a temp. range of 20° to 40° under anaerobic conditions. G. SKIRROW

**3090. Multi-purpose electro-analytical instrument incorporating an X-Y recorder.** A. J. Bard (Univ. of Texas, Austin, U.S.A.). *Anal. Chim. Acta*, 1959, **21** (4), 365-369.—The Moseley 3S X-Y recorder has a built-in time base, and the assembly also includes an electromechanical combination amperostat-potentiostat and a variable-speed polarising unit. Circuit diagrams are given. The necessity of correcting for *iR* drop is avoided, and the instru-

ment is used for voltametry, chronopotentiometry, coulometry and the recording of titration curves.

H. N. S.

**3091. Application of constant-current potentiometry to non-aqueous titrations of weak acids.** I. Shain and G. R. Svoboda (Univ. Wis., Madison, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1857-1860.—The electrode system consisted of two platinum indicator-electrodes and a fibre-type calomel reference electrode containing acetone saturated with LiCl in the outer compartment. The indicator electrodes were polarised by a constant 1-μA current. The potential was measured in three ways after each titration step—between the two platinum electrodes and between each platinum electrode and the reference electrode. By making all three measurements on the same soln. at the same point in the titration, erroneous displacement of the titration along the volume axis was eliminated. In most cases typical peak-shaped titration curves were obtained which permitted direct location of the end-point from the meter readings. Several weak acids were titrated with tetrabutylammonium hydroxide with acetone as solvent, reproducible results being obtained. G. P. COOK

**3092. Inexpensive high-frequency titration apparatus for general laboratory use. Applications to some EDTA and precipitation titrations.** V. Kyte and A. I. Vogel (Dept. of Chem., Woolwich Poly., London). *Analyst*, 1959, **84**, 647-654.—The construction of a stable high-frequency titrimeter that will respond to both over-all capacitance and over-all conductance changes in the titration cell is described. It is easily and inexpensively made. Examples of its use are given, including titration of metal ions with EDTA and precipitation titrations, e.g., SO<sub>4</sub><sup>2-</sup> with BaCl<sub>2</sub>, Th with Na oxalate, F<sup>-</sup> with La acetate and Be with NaOH.

A. O. JONES

**3093. Versatile Karl Fischer titrimeter.** F. B. Waddington (Res. Dept., Metropolitan-Vickers Electrical Co., Ltd.). *Lab. Practice*, 1959, **8** (8), 275-278.—A titrimeter for the determination of water by the Karl Fischer method is described and illustrated. The determination is made by direct titration, the end-point being detected by a meter with a scale deflection of 0 to 100 μA in conjunction with a pair of platinum electrodes and a variable potential of 0 to 136 mV. The titration vessel is such that very small vol. can be titrated, and rubber stoppers in elongated necks are used in preference to ground glass joints. Either a 25-ml or a 2-ml micro-burette may be used. Novel features include (i) a mechanical stirrer to enable immiscible liquids to be emulsified with CHCl<sub>3</sub> - methanol (5:2) during titration, (ii) a washing vessel, whereby an insol. solid can be repeatedly washed with solvent and the solvent returned to the titration vessel and titrated, and (iii) a graduated reservoir for sample liquids, directly connected with the titration vessel, to prevent ingress of air when the sample is introduced.

H. M.

**3094. Ion-exchange membranes in coulometry.** S. W. Feldberg and C. E. Bricker (Dept. of Chem., Princeton Univ., N.J., U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1852-1854.—Cation-exchange membranes have been used to separate the anode and cathode compartments during the coulometric determination of bases in both aqueous and non-aqueous media. These membranes replace the conventional

salt bridge or sintered glass discs and although not 100% permselective they are sufficiently selective to prevent the mixing of ions produced at the electrodes. Several applications are discussed.

K. A. PROCTOR

**3095. Direct-reading current integrator for coulometric analysis.** Shigeki Hanamura (Gov. Industrial Res. Inst., Nagoya, Japan). *Talanta*, 1959, **3** (1), 14-22.—The apparatus described and illustrated incorporates a bevel gear differential driven by a d.c. integrating motor. The instrument can be used in a constant-current apparatus (a timer then being unnecessary) or with a controlled-potential apparatus (chemical coulometer unnecessary). The high power-output permits coupling with recorders or mechanical counters. The coeff. of variation of counts per coulomb is approx. 0.3 to 0.4%.

J. P. STERN

**3096. Glove boxes of new design for work with radioactive substances.** N. I. Gusev, P. N. Palei, I. G. Sentyurin and I. S. Sklyarenko (V. I. Vernadskii Inst. of Geochem. and Anal. Chem., Acad. Sci. USSR, Moscow). *Zhur. Anal. Khim.*, 1959, **14** (5), 606-611.—A set of glove boxes comprising a working box, a centrifuge box and a weighing box are fitted with standard chambers for receiving a small closable box used for the transfer of chemicals and apparatus from one glove box to another.

C. D. KOPKIN

**3097. Preparation of suspended-solids samples for radioactivity counting.** R. L. Weatherford and T. E. Larson (Illinois State Water Survey, Urbana, U.S.A.). *Anal. Chem.*, 1959, **31** (11), 1931.—In using the alcohol burn-off method [Setter *et al.*, *Bull. A.S.T.M.*, 1958, (227), 35] to determine the activity of suspended matter in surface-water samples, difficulties have been experienced because of the indefinite counting area and losses during burning, handling and storing the sample. A technique for overcoming these problems, in which the Millipore filter is used as a binder, is described.

K. A. PROCTOR

**3098. Windowless gas-flow Geiger counter for the measurement of the radioactivity of chromatograms.** A. Benakis and B. Glisson (Inst. Therapeut., Univ., Genève). *Bull. Soc. Chim. Biol.*, 1959, **41** (9-10), 1289-1295.—The counter described, of 25 ml capacity, is designed to record low activities in <sup>14</sup>C-labelled biological materials. A slow stream of argon (99.9% pure) is bubbled through ethanol maintained at the temp. of melting ice, and passes

across the counting tube, the polished brass wall of which acts as the cathode, while the anode consists of a loop of platinum wire 15 mm in diam. The rectangular window opening may be 24 mm × 5 mm or 24 mm × 10 mm, and the weight of the apparatus (420 g) ensures sufficiently close contact with the chromatogram. The p.d. used is 1500 V and the dead time is 150 to 200  $\mu$ sec. Recording is by means of an integrator and a recording milliammeter. With this apparatus a fourfold increase in sensitivity was obtained in the measurement of labelled phenobarbitone, as compared with a conventional counter with a mica window of 1.9 mg per sq. cm, the chromatogram being moved at a rate of 2 cm per min.

S. BAAR

**3099. Methods of measurement of carbon-14 radioactivity.** R. Tykva and D. Grünberger (Lab. of Isotopes, Chem. Inst. Acad. Sci., Prague). *Chem. Listy*, 1959, **53** (9), 979-995.—A literature survey is presented covering papers, up to early 1959, concerning methods based on the detection of ionisation in gases, Geiger-Müller counters with thin end windows, windowless flow-counters, the preparation of samples, ionisation chambers, counters containing active gas, special ionisation methods and scintillation methods. (186 references.)

J. ŽYKA

**3100. Simple portable apparatus for the measurement of radioactivity of soft  $\beta$ -emitters.** R. Tykva (Isotope Lab., Chem. Inst. Acad. Sci., Prague). *Chem. Listy*, 1959, **53** (10), 1052-1053.—A simple portable apparatus for the measurement of the radioactivity of soft  $\beta$ -emitters consists of a changeable Geiger-Müller counter with a thin end-window (1.5 to 2.0 mg per sq. cm); it can be used for the rapid evaluation of activity on paper chromatograms and electropherograms.

J. ŽYKA

**3101. Mass-spectrometer inlet-system for the analysis of higher hydrocarbons.** C. Brunnée (Abteil. MAT, Atlas-Werke A.-G., Bremen). *Z. anal. Chem.*, 1959, **170** (1), 371-380.—In the device described, a Teflon membrane is pressed by a screw against a graduated capillary. The membrane serves both as a seal and as a pump. A combination of two inlet systems is shown, one operating up to 150° and the other up to 350°. The entire system, together with the head of the spectrometer, is housed in a thermostatically controlled enclosure. The influence of the design of the ion source on the resolving power, and the resolving power of double-focusing instruments are discussed. G. BURGER

# ERRATA

February (1960) issue, abstract 440, line 3. For W. F. Luk'yanov read V. F. Luk'yanov.  
February (1960) issue, abstract 558, line 3. For Zelentskaya read Zelenetskaya.  
April (1960) issue, abstract 1472, line 9. For

Calcium and Mg read Heavy metals.  
June (1960) issue, abstract 2272, line 9. For 0.05% read 0.5%.  
June (1960) issue, abstract 2458, line 5. For (24 8) read 42(8).



## ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	mμg
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	$\alpha_D^t$
coefficient	coeff.	ounce	oz
Colour Index	C.I.	parts per million	p.p.m.
concentrated	conc.	per cent.	%
concentration	concn.	per cent. (vol. in vol.)	% (v/v)
constant	const.	per cent. (wt. in vol.)	% (w/v)
crystalline	} cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	$\rho$	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	$n_D^t$
electromotive force	e.m.f.	relative band speed	$R_F$
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	$E_{1/2}$	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	$[\alpha]_D^t$
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μmole	watt	W
micron	μ	wavelength	λ
milliamper	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe<sup>II</sup>, Mo<sup>V</sup>. Substances in the ionic state are represented by Na<sup>+</sup>, Fe<sup>3+</sup>, Fe<sup>2+</sup>, etc., for cations and by Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, etc., for anions.

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